Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Solving the Schrödinger Equation of Hydrogen Molecule with the Free-Complement Variational Theory: Essentially Exact Potential Curves and Vibrational Levels of the Ground and Excited States of Π symmetry

Yusaku I. Kurokawa*, Hiroyuki Nakashima, and Hiroshi Nakatsuji*

*Quantum Chemistry Research Institute, The Kyoto Technoscience Center 16, 14 Yoshida Kawara-machi, Sakyo-Ku, Kyoto 606-8305, Japan*

* Electronic mail: y.kurokawa@qcri.or.jp and h.nakatsuji@qcri.or.jp

Table S1. The energies of the hydrogen molecule in the $^1\Pi_g$ state calculated with the Free Complement method at order $n = 3$.

| $R$ | $E_0$(I) | $E_1$(R) | $E_2$ | $E_3$ | $E_4$ | $E_5$ |
|---|---|---|---|---|---|---|
| 0.8 | -0.3602903 | -0.3358210 | -0.3231035 | -0.3208628 | -0.306779 | -0.295050 |
| 1.0 | -0.5076982 | -0.4831839 | -0.4707272 | -0.4681118 | -0.455366 | -0.442344 |
| 1.2 | -0.5850127 | -0.5604323 | -0.5481153 | -0.5454199 | -0.5335524 | -0.5201715 |
| 1.4 | -0.6263368 | -0.6016719 | -0.5894215 | -0.5867523 | -0.5754518 | -0.5622191 |
| 1.6 | -0.6473168 | -0.6225494 | -0.6103152 | -0.6077596 | -0.5967460 | -0.5842072 |
| 1.8 | -0.6568597 | -0.6319677 | -0.6197193 | -0.6173326 | -0.6064331 | -0.5948733 |
| 1.9 | -0.6588426 | -0.6338789 | -0.6216193 | -0.6193151 | -0.6084629 | -0.5973963 |
| 2.0 | -0.6595153 | -0.6344728 | -0.6222024 | -0.6199685 | -0.6091825 | -0.5985737 |
| 2.1 | -0.6591756 | -0.6340462 | -0.6217661 | -0.6195867 | -0.6088947 | -0.5986967 |
| 2.2 | -0.6580572 | -0.6328321 | -0.6205427 | -0.6184010 | -0.6078319 | -0.5979849 |
| 2.4 | -0.6541874 | -0.6287393 | -0.6164272 | -0.6143158 | -0.6040687 | -0.5947538 |
| 2.5 | -0.6517033 | -0.6261250 | -0.6137965 | -0.6116799 | -0.6016250 | -0.5924909 |
| 2.6 | -0.6489897 | -0.6232664 | -0.6109161 | -0.6087815 | -0.5989375 | -0.5899347 |
| 2.8 | -0.6431806 | -0.6171138 | -0.6046979 | -0.6024844 | -0.5931204 | -0.5842642 |
| 3.0 | -0.6372586 | -0.6107586 | -0.5982348 | -0.5958674 | -0.5870794 | -0.5782335 |
| 3.2 | -0.6315981 | -0.6045469 | -0.5918524 | -0.5892176 | -0.5811442 | -0.5721437 |
| 3.4 | -0.6265110 | -0.5987552 | -0.5857985 | -0.5827212 | -0.5755656 | -0.5661756 |
| 3.5 | -0.6242724 | -0.5960927 | -0.5829586 | -0.5795701 | -0.5729682 | -0.5632736 |
| 3.8 | -0.6191614 | -0.5893003 | -0.5753707 | -0.5706264 | -0.5659734 | -0.5550094 |
| 4.0 | -0.6172903 | -0.5857523 | -0.5710140 | -0.5651508 | -0.5617211 | -0.5509671 |
| 4.1 | -0.6168123 | -0.5841852 | -0.5689702 | -0.5625704 | -0.5596409 | -0.5491729 |
| 4.3 | -0.6166247 | -0.5812623 | -0.5650547 | -0.5577333 | -0.5555770 | -0.5456163 |
| 4.5 | -0.6171740 | -0.5784618 | -0.5613548 | -0.5533316 | -0.5517389 | -0.5423527 |
| 4.6 | -0.6176174 | -0.5770894 | -0.5596012 | -0.5512936 | -0.5499470 | -0.5409453 |
| 4.8 | -0.6186697 | -0.5744203 | -0.5563319 | -0.5475426 | -0.5467208 | -0.5389102 |
| 5.0 | -0.6197874 | -0.5718972 | -0.5534497 | -0.5443916 | -0.5440706 | -0.5380712 |
| 5.2 | -0.6208560 | -0.5695666 | -0.5510840 | -0.5431421 | -0.5412114 | -0.5372528 |
| 5.4 | -0.6218189 | -0.5674574 | -0.5494978 | -0.5429224 | -0.5386584 | -0.5356538 |
| 5.6 | -0.6226542 | -0.5655817 | -0.5490020 | -0.5424257 | -0.5364760 | -0.5337922 |
| 5.8 | -0.6233595 | -0.5639391 | -0.5493890 | -0.5413614 | -0.5346651 | -0.5320183 |
| 6.0 | -0.6239425 | -0.5625203 | -0.5501291 | -0.5400918 | -0.5332321 | -0.5304492 |
| 6.2 | -0.6244158 | -0.5613101 | -0.5509260 | -0.5388538 | -0.5321852 | -0.5291500 |
| 6.5 | -0.6249508 | -0.5598439 | -0.5520136 | -0.5372224 | -0.5313009 | -0.5280123 |
| 6.8 | -0.6253173 | -0.5587337 | -0.5529036 | -0.5359010 | -0.5310269 | -0.5281942 |
| 7.0 | -0.6254885 | -0.5581563 | -0.5533892 | -0.5351807 | -0.5310249 | -0.5286068 |
| 7.5 | -0.6257334 | -0.5571442 | -0.5542897 | -0.5338419 | -0.5312021 | -0.5295771 |
| 8.0 | -0.6258094 | -0.5565555 | -0.5548573 | -0.5329915 | -0.5313643 | -0.5302552 |
| 8.2 | -0.6258113 | -0.5563972 | -0.5550182 | -0.5327473 | -0.5314065 | -0.5304542 |
| 8.4 | -0.6258026 | -0.5562702 | -0.5551504 | -0.5325442 | -0.5314369 | -0.5306200 |
| 9.0 | -0.6257378 | -0.5560185 | -0.5554194 | -0.5321155 | -0.5314744 | -0.5309647 |
| 10.0 | -0.6255880 | -0.5558222 | -0.5556185 | -0.5317478 | -0.5314482 | -0.5312293 |
| 11.0 | -0.6254525 | -0.5557335 | -0.5556761 | -0.5315750 | -0.5313986 | -0.5313149 |
| 12.0 | -0.6253481 | -0.5556956 | -0.5556678 | -0.5314838 | -0.5313584 | -0.5313319 |
| 13.0 | -0.6252712 | -0.5556769 | -0.5556390 | -0.5314315 | -0.5313340 | -0.5313207 |
| 14.0 | -0.6252148 | -0.5556565 | -0.5556171 | -0.5313994 | -0.5313184 | -0.5313030 |
| 16.0 | -0.6251413 | -0.5556197 | -0.5555905 | -0.5313627 | -0.5312926 | -0.5312795 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 20.0 | -0.6250709 | -0.5555794 | -0.5555685 | -0.5313200 | -0.5312659 | -0.5312606 |

Table S2. The energy of the hydrogen molecule in the $^1\Pi_u$ state calculated with the Free Complement method at order $n = 3$.

| $R$ | $E_0$(C) | $E_1$(D) | $E_2$(V) | $E_3$(D') | $E_4$ | $E_5$ |
|---|---|---|---|---|---|---|
| 0.8 | -0.4261433 | -0.3589681 | -0.3357038 | -0.3352646 | -0.3236967 | -0.3214831 |
| 1.0 | -0.5725116 | -0.5059954 | -0.4830433 | -0.4824572 | -0.4710725 | -0.4690569 |
| 1.2 | -0.6486949 | -0.5828856 | -0.5602553 | -0.5595214 | -0.5482485 | -0.5463207 |
| 1.4 | -0.6888184 | -0.6237450 | -0.6014487 | -0.6005606 | -0.5893762 | -0.5875723 |
| 1.6 | -0.7085710 | -0.6442308 | -0.6222704 | -0.6212250 | -0.6101179 | -0.6085064 |
| 1.8 | -0.7168565 | -0.6532422 | -0.6316192 | -0.6304131 | -0.6193777 | -0.6180131 |
| 1.9 | -0.7182055 | -0.6549454 | -0.6334893 | -0.6322026 | -0.6212008 | -0.6199722 |
| 1.952 | -0.7183678 | -0.6552888 | -0.6339187 | -0.6325900 | -0.6216053 | -0.6204493 |
| 2.0 | -0.7182421 | -0.6553282 | -0.6340369 | -0.6326697 | -0.6217004 | -0.6206124 |
| 2.1 | -0.7172644 | -0.6546872 | -0.6335581 | -0.6321107 | -0.6211728 | -0.6202274 |
| 2.2 | -0.7155059 | -0.6532545 | -0.6322846 | -0.6307575 | -0.6198500 | -0.6190470 |
| 2.4 | -0.7103466 | -0.6487094 | -0.6280466 | -0.6263623 | -0.6155125 | -0.6149880 |
| 2.5 | -0.7072097 | -0.6458585 | -0.6253429 | -0.6235812 | -0.6127586 | -0.6123680 |
| 2.6 | -0.7038346 | -0.6427538 | -0.6223808 | -0.6205427 | -0.6097458 | -0.6094850 |
| 2.8 | -0.6966598 | -0.6360689 | -0.6159664 | -0.6139780 | -0.6032288 | -0.6032127 |
| 3.0 | -0.6892737 | -0.6290988 | -0.6092462 | -0.6071103 | -0.5966123 | -0.5964025 |
| 3.2 | -0.6819747 | -0.6221353 | -0.6025118 | -0.6002298 | -0.5899730 | -0.5895579 |
| 3.4 | -0.6749600 | -0.6153697 | -0.5959562 | -0.5935264 | -0.5834885 | -0.5828839 |
| 3.5 | -0.6716015 | -0.6121018 | -0.5927871 | -0.5902814 | -0.5803464 | -0.5796509 |
| 3.8 | -0.6622503 | -0.6028822 | -0.5838470 | -0.5810964 | -0.5714565 | -0.5704894 |
| 4.0 | -0.6566828 | -0.5972834 | -0.5784329 | -0.5754918 | -0.5660520 | -0.5648899 |
| 4.5 | -0.6452207 | -0.5853398 | -0.5670780 | -0.5634328 | -0.5546447 | -0.5528067 |
| 4.8 | -0.6399723 | -0.5795575 | -0.5619133 | -0.5575172 | -0.5494073 | -0.5468540 |
| 5.0 | -0.6370916 | -0.5762405 | -0.5592377 | -0.5540885 | -0.5466709 | -0.5433928 |
| 5.2 | -0.6346574 | -0.5733218 | -0.5572228 | -0.5510426 | -0.5445458 | -0.5403099 |
| 5.4 | -0.6326238 | -0.5707702 | -0.5558678 | -0.5483515 | -0.5429077 | -0.5375786 |
| 5.6 | -0.6309429 | -0.5685528 | -0.5550922 | -0.5459854 | -0.5415421 | -0.5351709 |
| 5.8 | -0.6295676 | -0.5666359 | -0.5547462 | -0.5439146 | -0.5402945 | -0.5330584 |
| 6.0 | -0.6284528 | -0.5649866 | -0.5546683 | -0.5421098 | -0.5391192 | -0.5312134 |
| 6.5 | -0.6265444 | -0.5618308 | -0.5549321 | -0.5385823 | -0.5365761 | -0.5293661 |
| 6.8 | -0.6258369 | -0.5604635 | -0.5551434 | -0.5370174 | -0.5353768 | -0.5295833 |
| 6.96 | -0.6255549 | -0.5598607 | -0.5552430 | -0.5363196 | -0.5348373 | -0.5297816 |
| 7.0 | -0.6254930 | -0.5597221 | -0.5552660 | -0.5361584 | -0.5347127 | -0.5298331 |
| 7.5 | -0.6249445 | -0.5583288 | -0.5554874 | -0.5345228 | -0.5334635 | -0.5304258 |
| 8.0 | -0.6246792 | -0.5574145 | -0.5556053 | -0.5334337 | -0.5326691 | -0.5308421 |
| 9.0 | -0.6245380 | -0.5564294 | -0.5556655 | -0.5322424 | -0.5318810 | -0.5312491 |
| 10.0 | -0.6245767 | -0.5560150 | -0.5556359 | -0.5317294 | -0.5315921 | -0.5313596 |
| 20.0 | -0.6249322 | -0.5555749 | -0.5555495 | -0.5313199 | -0.5312639 | -0.5312545 |

Table S3. The energy of the hydrogen molecule in the $^3\Pi_g$ state calculated with the Free Complement method at order $n = 3$.

| $R$ | $E_0$(i) | $E_1$(r) | $E_2$(w) | $E_3$(wa) | $E_4$(wb) | $E_5$ |
|---|---|---|---|---|---|---|
| 0.8 | -0.3603258 | -0.3358410 | -0.3231190 | -0.3207842 | -0.3068049 | -0.2947140 |
| 1.0 | -0.5077416 | -0.4832082 | -0.4707462 | -0.4679685 | -0.4553946 | -0.4416936 |
| 1.2 | -0.5850640 | -0.5604606 | -0.5481350 | -0.5453329 | -0.5335673 | -0.5197360 |
| 1.4 | -0.6263949 | -0.6017031 | -0.5894371 | -0.5867121 | -0.5754346 | -0.5619769 |
| 1.6 | -0.6473787 | -0.6225815 | -0.6103257 | -0.6077238 | -0.5966965 | -0.5839928 |
| 1.8 | -0.6569202 | -0.6319971 | -0.6197254 | -0.6172769 | -0.6063624 | -0.5946379 |
| 1.9 | -0.6588994 | -0.6339049 | -0.6216228 | -0.6192457 | -0.6083847 | -0.5971453 |
| 2.0 | -0.6595655 | -0.6344934 | -0.6222021 | -0.6198869 | -0.6090976 | -0.5983093 |
| 2.1 | -0.6592158 | -0.6340593 | -0.6217605 | -0.6194964 | -0.6088030 | -0.5984250 |
| 2.2 | -0.6580829 | -0.6328346 | -0.6205294 | -0.6183070 | -0.6077311 | -0.5977137 |
| 2.4 | -0.6541669 | -0.6287090 | -0.6163891 | -0.6142281 | -0.6039337 | -0.5945026 |
| 2.5 | -0.6516480 | -0.6260704 | -0.6137398 | -0.6116004 | -0.6014615 | -0.5922540 |
| 2.6 | -0.6488897 | -0.6231808 | -0.6108357 | -0.6087116 | -0.5987361 | -0.5897115 |
| 2.8 | -0.6429515 | -0.6169390 | -0.6045507 | -0.6024330 | -0.5928116 | -0.5840617 |
| 3.0 | -0.6368263 | -0.6104427 | -0.5979856 | -0.5958288 | -0.5866121 | -0.5780421 |
| 3.2 | -0.6308538 | -0.6040122 | -0.5914504 | -0.5891861 | -0.5804555 | -0.5719590 |
| 3.4 | -0.6253008 | -0.5978931 | -0.5851779 | -0.5826936 | -0.5746010 | -0.5659976 |
| 3.5 | -0.6227567 | -0.5950207 | -0.5822074 | -0.5795437 | -0.5718754 | -0.5630996 |
| 3.8 | -0.6164194 | -0.5875459 | -0.5743840 | -0.5706026 | -0.5651590 | -0.5548926 |
| 4.0 | -0.6135814 | -0.5838987 | -0.5705149 | -0.5651283 | -0.5620277 | -0.5527233 |
| 4.1 | -0.6126510 | -0.5825336 | -0.5689517 | -0.5625485 | -0.5604475 | -0.5511770 |
| 4.3 | -0.6117697 | -0.5804454 | -0.5659772 | -0.5577141 | -0.5568903 | -0.5476194 |
| 4.5 | -0.6119925 | -0.5786264 | -0.5628647 | -0.5533377 | -0.5531581 | -0.5440773 |
| 4.6 | -0.6123979 | -0.5776810 | -0.5612931 | -0.5514363 | -0.5512352 | -0.5424418 |
| 4.8 | -0.6135477 | -0.5756784 | -0.5582618 | -0.5481272 | -0.5474946 | -0.5396363 |
| 5.0 | -0.6148962 | -0.5736044 | -0.5555222 | -0.5453743 | -0.5441521 | -0.5377450 |
| 5.2 | -0.6162490 | -0.5715671 | -0.5532152 | -0.5434298 | -0.5412082 | -0.5367330 |
| 5.4 | -0.6175067 | -0.5696447 | -0.5514950 | -0.5424429 | -0.5386507 | -0.5356968 |
| 5.6 | -0.6186272 | -0.5678812 | -0.5505193 | -0.5419177 | -0.5364698 | -0.5342561 |
| 5.8 | -0.6196000 | -0.5662962 | -0.5502956 | -0.5412440 | -0.5346636 | -0.5326959 |
| 6.0 | -0.6204305 | -0.5648932 | -0.5505902 | -0.5403222 | -0.5332404 | -0.5312424 |
| 6.2 | -0.6211314 | -0.5636659 | -0.5511251 | -0.5392949 | -0.5322123 | -0.5300157 |
| 6.5 | -0.6219742 | -0.5621271 | -0.5520227 | -0.5378001 | -0.5313840 | -0.5288494 |
| 6.8 | -0.6226129 | -0.5609040 | -0.5528399 | -0.5364967 | -0.5311955 | -0.5287087 |
| 7.0 | -0.6229487 | -0.5602366 | -0.5533069 | -0.5357528 | -0.5312568 | -0.5289580 |
| 7.5 | -0.6235552 | -0.5589749 | -0.5542014 | -0.5342983 | -0.5315830 | -0.5297470 |
| 8.0 | -0.6239342 | -0.5581351 | -0.5547757 | -0.5333123 | -0.5318614 | -0.5303559 |
| 9.0 | -0.6243356 | -0.5571702 | -0.5553290 | -0.5322751 | -0.5320497 | -0.5309991 |
| 10.0 | -0.6245269 | -0.5566564 | -0.5555010 | -0.5321382 | -0.5317112 | -0.5312254 |
| 12.0 | -0.6247475 | -0.5560560 | -0.5555154 | -0.5319447 | -0.5313961 | -0.5312849 |
| 13.0 | -0.6247956 | -0.5558957 | -0.5555083 | -0.5318547 | -0.5313496 | -0.5312775 |
| 16.0 | -0.6248841 | -0.5556567 | -0.5554896 | -0.5316395 | -0.5312866 | -0.5312626 |
| 18.0 | -0.6249170 | -0.5556003 | -0.5554804 | -0.5315291 | -0.5312693 | -0.5312579 |
| 20.0 | -0.6249322 | -0.5555822 | -0.5555496 | -0.5314421 | -0.5312640 | -0.5312545 |

Table S4. The energy of the hydrogen molecule in the $^3\Pi_u$ state calculated with the Free Complement method at order $n = 3$.

| $R$ | $E_0$(c) | $E_1$(d) | $E_2$(k) | $E_3$(ka) | $E_4$(kb) | $E_5$ |
|---|---|---|---|---|---|---|
| 0.8 | -0.4407736 | -0.3633576 | -0.3371171 | -0.3357018 | -0.3247851 | -0.3213785 |
| 1.0 | -0.5884644 | -0.5107160 | -0.4844399 | -0.4830418 | -0.4722140 | -0.4689816 |
| 1.2 | -0.6657482 | -0.5878675 | -0.5616063 | -0.5602541 | -0.5494415 | -0.5462589 |
| 1.4 | -0.7067440 | -0.6289202 | -0.6027200 | -0.6014476 | -0.5906098 | -0.5875178 |
| 1.6 | -0.7271350 | -0.6495330 | -0.6234320 | -0.6222694 | -0.6113781 | -0.6084611 |
| 1.8 | -0.7358526 | -0.6586138 | -0.6326443 | -0.6316184 | -0.6206507 | -0.6179806 |
| 1.9 | -0.7373446 | -0.6603317 | -0.6344376 | -0.6334886 | -0.6224756 | -0.6199476 |
| 2.0 | -0.7374786 | -0.6607167 | -0.6349035 | -0.6340364 | -0.6229740 | -0.6205955 |
| 2.1 | -0.7365553 | -0.6600663 | -0.6343386 | -0.6335577 | -0.6224423 | -0.6202164 |
| 2.2 | -0.7348106 | -0.6586132 | -0.6329749 | -0.6322843 | -0.6211128 | -0.6190388 |
| 2.4 | -0.7295662 | -0.6539962 | -0.6285458 | -0.6280464 | -0.6167541 | -0.6149763 |
| 2.5 | -0.7263347 | -0.6510950 | -0.6257418 | -0.6253426 | -0.6139860 | -0.6123517 |
| 2.6 | -0.7228329 | -0.6479311 | -0.6226767 | -0.6223804 | -0.6109569 | -0.6094634 |
| 2.8 | -0.7153158 | -0.6411028 | -0.6160492 | -0.6159646 | -0.6044007 | -0.6031823 |
| 3.0 | -0.7074802 | -0.6339585 | -0.6092474 | -0.6091012 | -0.5975284 | -0.5965761 |
| 3.2 | -0.6996365 | -0.6267926 | -0.6025123 | -0.6021316 | -0.5906303 | -0.5899355 |
| 3.4 | -0.6919930 | -0.6197994 | -0.5959565 | -0.5953275 | -0.5838964 | -0.5834522 |
| 3.5 | -0.6882919 | -0.6164091 | -0.5927873 | -0.5920284 | -0.5806316 | -0.5803111 |
| 3.8 | -0.6778151 | -0.6067919 | -0.5838479 | -0.5826670 | -0.5714385 | -0.5713547 |
| 4.0 | -0.6714289 | -0.6009072 | -0.5784356 | -0.5769352 | -0.5660334 | -0.5656877 |
| 4.1 | -0.6684296 | -0.5981345 | -0.5759099 | -0.5742329 | -0.5635079 | -0.5630129 |
| 4.3 | -0.6628294 | -0.5929369 | -0.5712408 | -0.5691627 | -0.5588292 | -0.5579927 |
| 4.5 | -0.6577641 | -0.5882044 | -0.5671108 | -0.5645386 | -0.5546825 | -0.5534122 |
| 4.6 | -0.6554304 | -0.5860109 | -0.5652616 | -0.5623917 | -0.5528273 | -0.5512846 |
| 4.8 | -0.6511516 | -0.5819614 | -0.5620332 | -0.5584198 | -0.5496118 | -0.5473459 |
| 5.0 | -0.6473724 | -0.5783474 | -0.5595007 | -0.5548621 | -0.5471452 | -0.5438140 |
| 5.2 | -0.6440642 | -0.5751469 | -0.5577458 | -0.5516968 | -0.5454080 | -0.5406665 |
| 5.4 | -0.6411930 | -0.5723347 | -0.5567706 | -0.5488995 | -0.5440885 | -0.5378785 |
| 5.6 | -0.6387210 | -0.5698831 | -0.5564229 | -0.5464439 | -0.5428453 | -0.5354233 |
| 6.0 | -0.6348141 | -0.5659433 | -0.5566615 | -0.5424480 | -0.5403192 | -0.5314008 |
| 6.2 | -0.6332990 | -0.5643950 | -0.5569026 | -0.5408521 | -0.5391305 | -0.5298777 |
| 6.5 | -0.6314682 | -0.5625172 | -0.5571976 | -0.5388831 | -0.5375435 | -0.5293751 |
| 6.8 | -0.6300672 | -0.5610916 | -0.5573494 | -0.5373440 | -0.5362210 | -0.5297016 |
| 6.9 | -0.6296785 | -0.5607024 | -0.5573665 | -0.5369118 | -0.5358379 | -0.5298537 |
| 6.96 | -0.6294616 | -0.5604874 | -0.5573691 | -0.5366697 | -0.5356213 | -0.5299446 |
| 7.0 | -0.6293235 | -0.5603515 | -0.5573678 | -0.5365151 | -0.5354823 | -0.5300043 |
| 7.5 | -0.6279609 | -0.5590726 | -0.5571786 | -0.5349740 | -0.5340695 | -0.5306206 |
| 8.0 | -0.6270914 | -0.5583299 | -0.5568167 | -0.5339747 | -0.5331391 | -0.5309922 |
| 9.0 | -0.6261551 | -0.5574451 | -0.5562102 | -0.5328783 | -0.5321442 | -0.5313135 |
| 10.0 | -0.6257222 | -0.5568503 | -0.5559042 | -0.5323596 | -0.5317191 | -0.5313993 |
| 20.0 | -0.6250709 | -0.5555861 | -0.5555692 | -0.5314422 | -0.5312661 | -0.5312606 |

Table S5-1. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $E_0\ ^1\Pi_g$ state calculated from the PECs with the Free Complement method at order $n = 3$.

| $v$ | $\langle R \rangle$ | $\langle R^2 \rangle$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
|---|---|---|---|---|
| 0 | 1.10212 | 1.23020 | -143633.33 | |
| 1 | 1.17985 | 1.43973 | -141524.12 | 2109.20 |
| 2 | 1.26555 | 1.68472 | -139572.46 | 1951.66 |
| 3 | 1.36699 | 1.99215 | -137795.55 | 1776.91 |
| 4 | 1.51821 | 2.48228 | -136246.49 | 1549.06 |

a: Absolute energies in $cm^{-1}$.

Table S5-2. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $E_1\ ^1\Pi_g$ state calculated from the PECs with the Free Complement method at order $n = 3$.

| $v$ | $\langle R \rangle$ | $\langle R^2 \rangle$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
|---|---|---|---|---|
| 0 | 1.09646 | 1.21747 | -138117.08 | |
| 1 | 1.17077 | 1.41730 | -135963.77 | 2153.30 |
| 2 | 1.25027 | 1.64372 | -133952.69 | 2011.08 |
| 3 | 1.33831 | 1.90895 | -132089.29 | 1863.40 |
| 4 | 1.44210 | 2.23970 | -130389.72 | 1699.57 |
| 5 | 1.57300 | 2.68325 | -128886.05 | 1503.68 |
| 6 | 1.72539 | 3.24127 | -127601.80 | 1284.25 |
| 7 | 1.86164 | 3.79236 | -126484.57 | 1117.23 |
| 8 | 1.99339 | 4.36847 | -125466.46 | 1018.11 |
| 9 | 2.14437 | 5.06902 | -124544.14 | 922.33 |
| 10 | 2.32768 | 5.97548 | -123727.21 | 816.93 |
| 11 | 2.56749 | 7.25157 | -123031.57 | 695.63 |
| 12 | 2.92154 | 9.31949 | -122480.58 | 550.99 |
| 13 | 3.58235 | 13.78298 | -122110.64 | 369.93 |
| 14 | 5.51473 | 32.02194 | -121960.68 | 149.96 |

a: Absolute energies in $cm^{-1}$.

Table S5-3. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $E_2\ ^1\Pi_g$ state calculated from the PECs with the Free Complement method at order $n = 3$.

| $v$ | $\langle R \rangle$ | $\langle R^2 \rangle$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
|---|---|---|---|---|
| 0 | 1.09581 | 1.21601 | -135422.30 | |
| 1 | 1.16946 | 1.41406 | -133263.37 | 2158.92 |
| 2 | 1.24734 | 1.63590 | -131241.01 | 2022.37 |
| 3 | 1.33165 | 1.88985 | -129356.83 | 1884.18 |
| 4 | 1.42621 | 2.19091 | -127618.07 | 1738.76 |
| 5 | 1.53462 | 2.55674 | -126037.53 | 1580.55 |
| 6 | 1.65165 | 2.97902 | -124617.76 | 1419.77 |
| 7 | 1.76643 | 3.42547 | -123331.05 | 1286.71 |
| 8 | 1.88934 | 3.93482 | -122152.43 | 1178.62 |
| 9 | 2.07275 | 4.74141 | -121102.09 | 1050.34 |

a: Absolute energies in $cm^{-1}$.

Table S5-4. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $E_3\ ^1\Pi_g$ state calculated from the PECs with the Free Complement method at order $n$ = 3.

| $v$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
|---|---|---|---|---|
| 0 | 1.09831 | 1.22145 | -134932.46 | |
| 1 | 1.17030 | 1.41590 | -132768.62 | 2163.84 |
| 2 | 1.24544 | 1.63067 | -130734.05 | 2034.57 |
| 3 | 1.32418 | 1.86854 | -128823.56 | 1910.48 |
| 4 | 1.40716 | 2.13325 | -127032.64 | 1790.93 |
| 5 | 1.49503 | 2.42917 | -125357.84 | 1674.80 |
| 6 | 1.58867 | 2.76210 | -123797.22 | 1560.62 |
| 7 | 1.68953 | 3.14084 | -122349.93 | 1447.29 |
| 8 | 1.80124 | 3.58400 | -121017.21 | 1332.73 |
| 9 | 1.95173 | 4.21434 | -119814.70 | 1202.50 |
| 10 | 2.36369 | 6.05492 | -118889.01 | 925.70 |
| 11 | 2.52000 | 6.94357 | -118321.80 | 567.21 |
| 12 | 2.75389 | 8.27340 | -117685.63 | 636.17 |
| 13 | 3.04960 | 10.17118 | -117205.81 | 479.83 |
| 14 | 3.65247 | 14.36473 | -116858.52 | 347.28 |
| 15 | 4.85601 | 24.92282 | -116672.42 | 186.11 |
| 16 | 7.61263 | 60.95268 | -116617.20 | 55.22 |
| 17 | 11.70201 | 146.20350 | -116603.86 | 13.33 |
| 18 | 18.21704 | 357.91710 | -116598.90 | 4.96 |
| 19 | 28.80516 | 900.14483 | -116597.01 | 1.89 |

a: Absolute energies in $cm^{-1}$.

Table S5-5. Vibrational Energy levels $E_v$ of the $E_4$ and $E_5$ $^1\Pi_g$ states calculated from the PECs with the Free Complement method at order $n = 3$.

| | $E_4$ | | | | $E_5$ | | | |
|---|---|---|---|---|---|---|---|---|
| $v$ | $\langle R \rangle$ | $\langle R^2 \rangle$ | $E_v$ [a] | $E_v$-$E_{v-1}$ | $\langle R \rangle$ | $\langle R^2 \rangle$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
| 0 | 1.10519 | 1.23706 | -132596.26 | | 1.12675 | 1.28553 | -130333.51 | |
| 1 | 1.18226 | 1.44550 | -130497.20 | 2099.06 | 1.19999 | 1.48873 | -128275.55 | 2057.96 |
| 2 | 1.26453 | 1.68162 | -128539.89 | 1957.32 | 1.27806 | 1.71736 | -126343.59 | 1931.95 |
| 3 | 1.35511 | 1.95722 | -126729.97 | 1809.92 | 1.36058 | 1.97293 | -124537.39 | 1806.21 |
| 4 | 1.45784 | 2.28875 | -125077.88 | 1652.08 | 1.44896 | 2.26231 | -122852.02 | 1685.36 |
| 5 | 1.56926 | 2.67276 | -123587.32 | 1490.56 | 1.55614 | 2.63120 | -121298.55 | 1553.47 |
| 6 | 1.67599 | 3.06964 | -122229.45 | 1357.87 | 1.70030 | 3.15361 | -119932.25 | 1366.30 |
| 7 | 1.78432 | 3.49933 | -120969.54 | 1259.91 | 1.84838 | 3.74436 | -118752.72 | 1179.53 |
| 8 | 1.91289 | 4.03547 | -119814.22 | 1155.33 | 2.14251 | 4.98645 | -117794.94 | 957.78 |
| 9 | 2.05575 | 4.66902 | -118778.83 | 1035.39 | 2.28088 | 5.69594 | -117088.02 | 706.92 |
| 10 | 2.19496 | 5.33825 | -117840.79 | 938.04 | 2.42938 | 6.51090 | -116341.24 | 746.78 |
| 11 | 2.44057 | 6.57037 | -117019.04 | 821.75 | | | | |

a: Absolute energies in $cm^{-1}$.

Table S6-1. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $E_0\ ^1\Pi_u$ state calculated from the PECs with the Free Complement method at order $n = 3$ and comparison with other studies.

| | | FC method | | | Ref. (theoretical)[b] | Ref. (experimental)[c] |
|---|---|---|---|---|---|---|
| $v$ | $\langle R \rangle$ | $\langle R^2 \rangle$ | $E_v$ [a] | $E_v$-$E_{v-1}$ | $E_v$-$E_{v-1}$ | $E_v$-$E_{v-1}$ |
| 0 | 1.06675 | 1.15220 | -156453.28 | | | |
| 1 | 1.13572 | 1.33325 | -154145.20 | 2308.08 | 2310.62 | 2308.67 |
| 2 | 1.20781 | 1.53332 | -151971.81 | 2173.39 | 2176.04 | 2174.67 |
| 3 | 1.28385 | 1.75607 | -149929.62 | 2042.19 | 2044.98 | 2043.14 |
| 4 | 1.36474 | 2.00603 | -148016.24 | 1913.38 | 1915.03 | 1913.07 |
| 5 | 1.45140 | 2.28874 | -146231.31 | 1784.94 | 1789.08 | 1783.87 |
| 6 | 1.54538 | 2.61250 | -144576.13 | 1655.18 | 1655.81 | 1654.33 |
| 7 | 1.64904 | 2.99002 | -143053.42 | 1522.70 | 1523.20 | 1522.56 |
| 8 | 1.76602 | 3.44107 | -141667.79 | 1385.63 | 1386.41 | 1386.09 |
| 9 | 1.90217 | 3.99862 | -140425.98 | 1241.81 | 1242.75 | 1242.27 |
| 10 | 2.06797 | 4.72343 | -139338.68 | 1087.30 | 1088.54 | 1087.85 |
| 11 | 2.28274 | 5.73571 | -138421.43 | 917.24 | | |
| 12 | 2.59278 | 7.34115 | -137698.08 | 723.35 | | |
| 13 | 3.17123 | 10.80733 | -137208.95 | 489.13 | | |

a: Absolute energies in $cm^{-1}$.

b: Ref. W. Kolos, L. Wolniewicz, *J. Chem. Phys.*, 1968, **48**, 3672

c: Ref. G. Herzberg and A. Monfils, *J. Mol. Spectry.*, 1960, **5**, 482.

Table S6-2. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $E_1\ ^1\Pi_u$ state calculated from the PECs with the Free Complement method at order $n = 3$.

| $v$ | $\langle R \rangle$ | $\langle R^2 \rangle$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
|---|---|---|---|---|
| 0 | 1.08419 | 1.19022 | -142663.59 | |
| 1 | 1.15484 | 1.37863 | -140437.84 | 2225.75 |
| 2 | 1.22842 | 1.58624 | -138342.13 | 2095.71 |
| 3 | 1.30559 | 1.81626 | -136372.12 | 1970.01 |
| 4 | 1.38713 | 2.07269 | -134524.21 | 1847.91 |
| 5 | 1.47369 | 2.36000 | -132796.06 | 1728.16 |
| 6 | 1.56624 | 2.68429 | -131186.66 | 1609.39 |
| 7 | 1.66620 | 3.05422 | -129695.85 | 1490.82 |
| 8 | 1.77552 | 3.48179 | -128324.26 | 1371.58 |
| 9 | 1.89707 | 3.98493 | -127073.27 | 1251.00 |
| 10 | 2.03512 | 4.59099 | -125945.64 | 1127.62 |
| 11 | 2.19560 | 5.34112 | -124945.05 | 1000.60 |
| 12 | 2.38826 | 6.30549 | -124076.61 | 868.43 |
| 13 | 2.62895 | 7.60728 | -123346.65 | 729.96 |
| 14 | 2.94700 | 9.49241 | -122762.50 | 584.15 |
| 15 | 3.40666 | 12.55207 | -122331.89 | 430.60 |
| 16 | 4.21513 | 18.92819 | -122062.97 | 268.93 |
| 17 | 6.09922 | 39.01924 | -121956.70 | 106.26 |
| 18 | 11.22573 | 136.04824 | -121932.08 | 24.62 |

a: Absolute energies in $cm^{-1}$.

Table S6-3. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $E_2\ ^1\Pi_u$ state calculated from the PECs with the Free Complement method at order $n = 3$.

| $v$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
|---|---|---|---|---|
| 0 | 1.09306 | 1.20983 | -138009.42 | |
| 1 | 1.16489 | 1.40284 | -135826.74 | 2182.68 |
| 2 | 1.23974 | 1.61575 | -133773.34 | 2053.40 |
| 3 | 1.31830 | 1.85193 | -131845.01 | 1928.32 |
| 4 | 1.40146 | 2.11590 | -130038.41 | 1806.60 |
| 5 | 1.49020 | 2.41322 | -128351.65 | 1686.77 |
| 6 | 1.58604 | 2.75237 | -126784.88 | 1566.77 |
| 7 | 1.69201 | 3.14854 | -125340.81 | 1444.08 |

a: Absolute energies in $cm^{-1}$.

Table S6-4. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $E_3\ ^1\Pi_u$ state calculated from the PECs with the Free Complement method at order $n = 3$.

| $v$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
|---|---|---|---|---|
| 0 | 1.08860 | 1.19995 | -137698.79 | |
| 1 | 1.15967 | 1.39022 | -135493.19 | 2205.60 |
| 2 | 1.23361 | 1.59972 | -133416.40 | 2076.79 |
| 3 | 1.31104 | 1.83149 | -131463.84 | 1952.56 |
| 4 | 1.39268 | 2.08939 | -129631.60 | 1832.24 |
| 5 | 1.47913 | 2.37758 | -127916.87 | 1714.74 |
| 6 | 1.57122 | 2.70161 | -126318.08 | 1598.79 |
| 7 | 1.67015 | 3.06917 | -124834.37 | 1483.71 |
| 8 | 1.77752 | 3.49055 | -123465.53 | 1368.84 |
| 9 | 1.89564 | 3.98078 | -122211.81 | 1253.72 |
| 10 | 2.02779 | 4.56165 | -121074.54 | 1137.27 |
| 11 | 2.17823 | 5.26408 | -120055.45 | 1019.09 |
| 12 | 2.35376 | 6.13823 | -119157.25 | 898.20 |
| 13 | 2.56502 | 7.26731 | -118383.59 | 773.66 |
| 14 | 2.83113 | 8.80797 | -117739.56 | 644.03 |
| 15 | 3.19014 | 11.09459 | -117232.08 | 507.48 |
| 16 | 3.73605 | 15.03595 | -116870.12 | 361.96 |
| 17 | 5.31433 | 29.74075 | -116676.63 | 193.49 |
| 18 | 7.05540 | 52.70914 | -116636.26 | 40.38 |
| 19 | 8.59467 | 78.87408 | -116607.50 | 28.75 |
| 20 | 10.04126 | 108.56512 | -116584.82 | 22.68 |

a: Absolute energies in $cm^{-1}$.

Table S6-5. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $E_4\ ^1\Pi_u$ state calculated from the PECs with the Free Complement method at order $n = 3$.

| $v$ | $\langle R \rangle$ | $\langle R^2 \rangle$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
|---|---|---|---|---|
| 0 | 1.09034 | 1.20378 | -135294.76 | |
| 1 | 1.16187 | 1.39556 | -133097.41 | 2197.36 |
| 2 | 1.23809 | 1.61146 | -131034.34 | 2063.07 |
| 3 | 1.31902 | 1.85376 | -129109.88 | 1924.46 |
| 4 | 1.40167 | 2.11653 | -127309.26 | 1800.62 |
| 5 | 1.49105 | 2.41578 | -125626.77 | 1682.49 |
| 6 | 1.58607 | 2.75253 | -124063.13 | 1563.64 |
| 7 | 1.69132 | 3.14611 | -122620.25 | 1442.89 |
| 8 | 1.81217 | 3.62401 | -121304.19 | 1316.06 |
| 9 | 1.96501 | 4.26457 | -120133.57 | 1170.62 |
| 10 | 2.18405 | 5.24662 | -119149.06 | 984.51 |
| 11 | 2.44149 | 6.52080 | -118377.71 | 771.35 |
| 12 | 2.67213 | 7.81410 | -117742.00 | 635.71 |
| 13 | 3.00043 | 9.80461 | -117221.53 | 520.46 |
| 14 | 3.54289 | 13.52256 | -116845.34 | 376.19 |
| 15 | 4.85029 | 24.83872 | -116648.74 | 196.60 |

a: Absolute energies in $cm^{-1}$.

Table S6-6. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $E_5$ $^1\Pi_u$ state calculated from the PECs with the Free Complement method at order $n$ = 3.

| $v$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
|---|---|---|---|---|
| 0 | 1.09817 | 1.22120 | -135077.59 | |
| 1 | 1.17006 | 1.41537 | -132920.00 | 2157.59 |
| 2 | 1.24295 | 1.62420 | -130882.77 | 2037.23 |
| 3 | 1.31854 | 1.85289 | -128953.62 | 1929.15 |
| 4 | 1.40088 | 2.11432 | -127140.56 | 1813.06 |
| 5 | 1.48669 | 2.40250 | -125443.10 | 1697.47 |
| 6 | 1.57924 | 2.72971 | -123859.18 | 1583.92 |
| 7 | 1.67799 | 3.09863 | -122387.98 | 1471.21 |
| 8 | 1.78517 | 3.52145 | -121029.94 | 1358.03 |
| 9 | 1.90306 | 4.01286 | -119784.61 | 1245.33 |
| 10 | 2.03440 | 4.59271 | -118653.33 | 1131.29 |
| 11 | 2.18435 | 5.29562 | -117637.90 | 1015.43 |
| 12 | 2.38365 | 6.29357 | -116747.52 | 890.38 |

a: Absolute energies in $cm^{-1}$.

Table S7-1. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $^3\Pi_g$ states calculated from the PECs with the Free Complement method at order $n$ = 3.

| | $E_0$(a) | | | | $E_1$(r) | | | |
|---|---|---|---|---|---|---|---|---|
| $v$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
| 0 | 1.10117 | 1.22802 | -143639.82 | | 1.09582 | 1.21601 | -138118.69 | |
| 1 | 1.17722 | 1.43316 | -141517.56 | 2122.26 | 1.16912 | 1.41321 | -135956.91 | 2161.78 |
| 2 | 1.25913 | 1.66738 | -139542.01 | 1975.55 | 1.24652 | 1.63370 | -133930.97 | 2025.94 |
| 3 | 1.35084 | 1.94514 | -137719.89 | 1822.12 | 1.33006 | 1.88538 | -132041.41 | 1889.56 |
| 4 | 1.46395 | 2.30827 | -136072.66 | 1647.23 | 1.42497 | 2.18731 | -130296.23 | 1745.18 |
| 5 | 1.67589 | 3.04046 | -134684.93 | 1387.72 | 1.54794 | 2.60069 | -128725.07 | 1571.16 |
| 6 | | | | | 1.74303 | 3.30121 | -127412.77 | 1312.30 |
| 7 | | | | | 1.94829 | 4.12370 | -126412.83 | 999.94 |
| 8 | | | | | 2.06525 | 4.67500 | -125514.64 | 898.19 |
| 9 | | | | | 2.22419 | 5.43818 | -124683.94 | 830.70 |
| 10 | | | | | 2.41200 | 6.40436 | -123943.66 | 740.28 |
| 11 | | | | | 2.65589 | 7.75212 | -123310.93 | 632.73 |
| 12 | | | | | 2.99234 | 9.78606 | -122800.87 | 510.05 |
| 13 | | | | | 3.48908 | 13.17323 | -122427.75 | 373.13 |
| 14 | | | | | 4.22143 | 19.05449 | -122191.10 | 236.65 |
| 15 | | | | | 5.09549 | 27.65639 | -122051.29 | 139.81 |
| 16 | | | | | 6.44869 | 44.12143 | -121968.31 | 82.98 |
| 17 | | | | | 10.39874 | 115.44327 | -121933.48 | 34.83 |

a: Absolute energies in $cm^{-1}$.

Table S7-2. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $^3\Pi_g$ states calculated from the PECs with the Free Complement method at order $n$ = 3.

| | $E_2$(w) | | | | $E_3$(wa) | | | |
|---|---|---|---|---|---|---|---|---|
| $v$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
| 0 | 1.09533 | 1.21492 | -135420.13 | | 1.09805 | 1.22090 | -134915.17 | |
| 1 | 1.16823 | 1.41102 | -133254.94 | 2165.18 | 1.17044 | 1.41625 | -132753.86 | 2161.30 |
| 2 | 1.24471 | 1.62888 | -131221.92 | 2033.02 | 1.24569 | 1.63134 | -130721.47 | 2032.39 |
| 3 | 1.32637 | 1.87485 | -129320.15 | 1901.77 | 1.32443 | 1.86926 | -128812.44 | 1909.04 |
| 4 | 1.41735 | 2.16406 | -127554.38 | 1765.78 | 1.40742 | 2.13403 | -127022.46 | 1789.98 |
| 5 | 1.52988 | 2.54126 | -125946.92 | 1607.46 | 1.49531 | 2.43006 | -125348.36 | 1674.10 |
| 6 | 1.68165 | 3.08113 | -124552.36 | 1394.56 | 1.58905 | 2.76339 | -123788.37 | 1559.99 |
| 7 | 1.82062 | 3.62567 | -123369.92 | 1182.44 | 1.69089 | 3.14579 | -122342.40 | 1445.97 |
| 8 | 1.93285 | 4.11280 | -122274.67 | 1095.26 | 1.80954 | 3.61557 | -121017.08 | 1325.32 |
| 9 | 2.13653 | 5.02713 | -121295.35 | 979.31 | 1.97537 | 4.30850 | -119843.70 | 1173.38 |
| 10 | | | | | 2.29918 | 5.77043 | -118915.48 | 928.22 |
| 11 | | | | | 2.61496 | 7.40321 | -118322.04 | 593.44 |
| 12 | | | | | 2.75927 | 8.33242 | -117747.11 | 574.93 |
| 13 | | | | | 3.08483 | 10.37877 | -117277.43 | 469.68 |
| 14 | | | | | 3.61631 | 14.12036 | -116917.38 | 360.05 |
| 15 | | | | | 5.38792 | 30.17480 | -116749.39 | 167.99 |
| 16 | | | | | 6.44457 | 44.16651 | -116692.03 | 57.36 |
| 17 | | | | | 7.63511 | 62.77825 | -116652.53 | 39.50 |
| 18 | | | | | 9.43419 | 95.94119 | -116623.75 | 28.79 |
| 19 | | | | | 12.49093 | 167.18986 | -116607.02 | 16.73 |
| 20 | | | | | 17.75552 | 336.79596 | -116599.25 | 7.77 |
| 21 | | | | | 28.68315 | 882.52147 | -116596.54 | 2.72 |

a: Absolute energies in $cm^{-1}$.

Table S7-3. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $^3\Pi_g$ states calculated from the PECs with the Free Complement method at order $n$ = 3.

| | $E_4$(wb) | | | | $E_5$ | | | |
|---|---|---|---|---|---|---|---|---|
| $v$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
| 0 | 1.10437 | 1.23518 | -132574.76 | | 1.12677 | 1.28561 | -130277.22 | |
| 1 | 1.17998 | 1.43983 | -130465.85 | 2108.91 | 1.20034 | 1.48963 | -128224.48 | 2052.74 |
| 2 | 1.25977 | 1.66884 | -128490.43 | 1975.42 | 1.27841 | 1.71833 | -126295.23 | 1929.25 |
| 3 | 1.34669 | 1.93298 | -126652.30 | 1838.13 | 1.36085 | 1.97373 | -124490.25 | 1804.98 |
| 4 | 1.45014 | 2.26501 | -124967.61 | 1684.70 | 1.45165 | 2.27101 | -122806.70 | 1683.55 |
| 5 | 1.58877 | 2.73591 | -123485.11 | 1482.50 | 1.58916 | 2.74064 | -121289.06 | 1517.63 |
| 6 | 1.72208 | 3.23006 | -122222.68 | 1262.43 | 1.75891 | 3.36038 | -120060.52 | 1228.55 |
| 7 | 1.79903 | 3.55809 | -121030.12 | 1192.56 | 1.82505 | 3.66669 | -118904.55 | 1155.97 |
| 8 | 1.90591 | 4.01142 | -119878.76 | 1151.37 | 2.07911 | 4.72393 | -117884.44 | 1020.11 |
| 9 | 2.02931 | 4.56388 | -118812.37 | 1066.39 | 2.33413 | 5.93229 | -117124.28 | 760.16 |
| 10 | 2.19568 | 5.34075 | -117853.94 | 958.43 | 2.45504 | 6.65783 | -116449.38 | 674.90 |
| 11 | 2.43619 | 6.55318 | -117033.07 | 820.87 | | | | |

a: Absolute energies in $cm^{-1}$.

Table S8-1. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $^3\Pi_u$ states calculated from the PECs with the Free Complement method at order $n = 3$.

| | $E_0$ | | | | $E_1$ | | | |
|---|---|---|---|---|---|---|---|---|
| $v$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
| 0 | 1.06977 | 1.15846 | -160654.69 | | 1.08358 | 1.18879 | -143839.01 | |
| 1 | 1.13562 | 1.33237 | -158313.62 | 2341.07 | 1.15299 | 1.37401 | -141596.00 | 2243.01 |
| 2 | 1.20376 | 1.52217 | -156095.44 | 2218.19 | 1.22501 | 1.57715 | -139479.15 | 2116.85 |
| 3 | 1.27479 | 1.73039 | -153995.96 | 2099.48 | 1.30020 | 1.80094 | -137483.80 | 1995.35 |
| 4 | 1.34925 | 1.95993 | -152011.73 | 1984.24 | 1.37919 | 2.04876 | -135605.94 | 1877.87 |
| 5 | 1.42754 | 2.21374 | -150140.88 | 1870.84 | 1.46247 | 2.32413 | -133842.74 | 1763.20 |
| 6 | 1.51035 | 2.49610 | -148382.84 | 1758.04 | 1.55073 | 2.63174 | -132192.65 | 1650.08 |
| 7 | 1.59870 | 2.81296 | -146737.68 | 1645.16 | 1.64504 | 2.97822 | -130654.81 | 1537.84 |
| 8 | 1.69414 | 3.17296 | -145206.32 | 1531.36 | 1.74690 | 3.37279 | -129229.13 | 1425.68 |
| 9 | 1.79877 | 3.58833 | -143790.54 | 1415.78 | 1.85844 | 3.82867 | -127916.26 | 1312.87 |
| 10 | 1.91567 | 4.07735 | -142493.27 | 1297.27 | 1.98286 | 4.36581 | -126717.99 | 1198.27 |
| 11 | 2.04922 | 4.66771 | -141319.04 | 1174.22 | 2.12491 | 5.01522 | -125637.53 | 1080.46 |
| 12 | 2.20636 | 5.40469 | -140274.29 | 1044.75 | 2.29241 | 5.82943 | -124680.25 | 957.28 |
| 13 | 2.39832 | 6.36620 | -139367.65 | 906.64 | 2.49974 | 6.90798 | -123854.61 | 825.64 |
| 14 | 2.64471 | 7.69824 | -138610.12 | 757.53 | 2.77861 | 8.47927 | -123174.49 | 680.12 |
| 15 | 2.98262 | 9.70505 | -138014.44 | 595.68 | 3.21696 | 11.22296 | -122665.38 | 509.11 |
| 16 | 3.48943 | 13.11573 | -137592.18 | 422.26 | 3.88507 | 16.10270 | -122351.03 | 314.35 |
| 17 | 4.34630 | 20.04389 | -137343.51 | 248.67 | 4.50574 | 21.64113 | -122156.16 | 194.87 |
| 18 | 5.82149 | 35.58289 | -137236.84 | 106.67 | 5.39361 | 30.96389 | -122018.67 | 137.49 |
| 19 | 7.99747 | 67.48117 | -137193.30 | 43.55 | 7.30708 | 56.38861 | -121950.51 | 68.16 |
| 20 | 12.01756 | 153.64293 | -137177.09 | 16.21 | 13.79958 | 207.08950 | -121931.22 | 19.29 |
| 21 | 21.30444 | 490.07860 | -137172.45 | 4.64 | | | | |

a: Absolute energies in $cm^{-1}$.

Table S8-2. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $^3\Pi_u$ states calculated from the PECs with the Free Complement method at order $n = 3$.

| | $E_2$ | | | | $E_3$ | | | |
|---|---|---|---|---|---|---|---|---|
| $v$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
| 0 | 1.08821 | 1.19904 | -138185.75 | | 1.09306 | 1.20982 | -138009.29 | |
| 1 | 1.15891 | 1.38834 | -135972.62 | 2213.13 | 1.16466 | 1.40224 | -135826.14 | 2183.16 |
| 2 | 1.23375 | 1.60003 | -133890.82 | 2081.80 | 1.23776 | 1.61051 | -133767.57 | 2058.56 |
| 3 | 1.31394 | 1.83939 | -131944.68 | 1946.14 | 1.31266 | 1.83618 | -131820.59 | 1946.99 |
| 4 | 1.39723 | 2.10281 | -130127.65 | 1817.03 | 1.39302 | 2.09060 | -129985.00 | 1835.59 |
| 5 | 1.48604 | 2.39939 | -128431.12 | 1696.53 | 1.47783 | 2.37377 | -128263.88 | 1721.12 |
| 6 | 1.58175 | 2.73712 | -126856.33 | 1574.79 | 1.56805 | 2.69129 | -126654.48 | 1609.40 |
| 7 | 1.68775 | 3.13225 | -125405.26 | 1451.08 | 1.66455 | 3.04956 | -125156.52 | 1497.96 |
| 8 | 1.81187 | 3.62155 | -124086.58 | 1318.67 | 1.76885 | 3.45813 | -123769.81 | 1386.71 |
| 9 | 1.98605 | 4.35092 | -122928.27 | 1158.32 | 1.88313 | 3.93070 | -122494.67 | 1275.14 |
| 10 | 3.63374 | 13.51697 | -122215.32 | 712.95 | 2.01034 | 4.48697 | -121332.34 | 1162.34 |
| 11 | 3.23203 | 11.69536 | -122074.69 | 140.63 | 2.15500 | 5.15749 | -120285.27 | 1047.06 |
| 12 | 4.67476 | 23.79318 | -121977.39 | 97.31 | 2.32447 | 5.99307 | -119357.59 | 927.68 |
| 13 | 8.09134 | 70.29240 | -121935.41 | 41.98 | 2.53134 | 7.08491 | -118555.74 | 801.86 |
| 14 | | | | | 2.79879 | 8.61167 | -117889.28 | 666.45 |
| 15 | | | | | 3.17135 | 10.95564 | -117370.64 | 518.65 |
| 16 | | | | | 3.73621 | 15.00880 | -117010.29 | 360.35 |
| 17 | | | | | 4.68682 | 23.27032 | -116803.53 | 206.76 |
| 18 | | | | | 5.94656 | 37.28891 | -116709.19 | 94.34 |
| 19 | | | | | 7.50486 | 59.55250 | -116657.03 | 52.15 |
| 20 | | | | | 9.58259 | 97.51703 | -116628.10 | 28.93 |
| 21 | | | | | 12.44887 | 165.24211 | -116612.26 | 15.84 |
| 22 | | | | | 16.50742 | 291.49190 | -116603.84 | 8.42 |
| 23 | | | | | 22.41558 | 538.84964 | -116599.54 | 4.30 |

a: Absolute energies in $cm^{-1}$.

Table S8-3. Vibrational Energy levels $E_v$ ($cm^{-1}$) of the $^3\Pi_u$ states calculated from the PECs with the Free Complement method at order $n = 3$.

| | $E_4$ | | | | $E_5$ | | | |
|---|---|---|---|---|---|---|---|---|
| $v$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ | $<R>$ | $<R^2>$ | $E_v$ [a] | $E_v$-$E_{v-1}$ |
| 0 | 1.09006 | 1.20314 | -135572.20 | | 1.09836 | 1.22161 | -135073.65 | |
| 1 | 1.16097 | 1.39330 | -133369.40 | 2202.80 | 1.17037 | 1.41615 | -132915.35 | 2158.30 |
| 2 | 1.23466 | 1.60237 | -131294.04 | 2075.36 | 1.24553 | 1.63101 | -130884.23 | 2031.12 |
| 3 | 1.31171 | 1.83328 | -129341.47 | 1952.58 | 1.32433 | 1.86911 | -128976.23 | 1908.00 |
| 4 | 1.39294 | 2.09012 | -127507.74 | 1833.73 | 1.40740 | 2.13409 | -127187.58 | 1788.66 |
| 5 | 1.48004 | 2.38045 | -125791.57 | 1716.18 | 1.49424 | 2.42676 | -125513.76 | 1673.81 |
| 6 | 1.57678 | 2.72003 | -124198.55 | 1593.02 | 1.58350 | 2.74503 | -123946.51 | 1567.25 |
| 7 | 1.68430 | 3.11898 | -122737.63 | 1460.92 | 1.67929 | 3.10470 | -122480.11 | 1466.40 |
| 8 | 1.80627 | 3.59941 | -121409.91 | 1327.72 | 1.78592 | 3.52553 | -121122.40 | 1357.72 |
| 9 | 1.97435 | 4.29942 | -120240.77 | 1169.14 | 1.90106 | 4.00666 | -119874.40 | 1248.00 |
| 10 | 2.23493 | 5.46811 | -119298.88 | 941.89 | 2.03079 | 4.57889 | -118737.45 | 1136.95 |
| 11 | 2.45934 | 6.61372 | -118578.16 | 720.72 | 2.17805 | 5.26845 | -117714.08 | 1023.37 |
| 12 | 2.66075 | 7.75832 | -117935.96 | 642.19 | 2.36698 | 6.21179 | -116812.60 | 901.48 |
| 13 | 2.95596 | 9.54427 | -117401.06 | 534.90 | | | | |
| 14 | 3.40205 | 12.53582 | -116990.83 | 410.23 | | | | |
| 15 | 4.20355 | 18.86142 | -116729.18 | 261.65 | | | | |
| 16 | 6.04312 | 38.37719 | -116621.55 | 107.63 | | | | |
| 17 | 11.82658 | 152.66189 | -116597.04 | 24.51 | | | | |

a: Absolute energies in $cm^{-1}$.

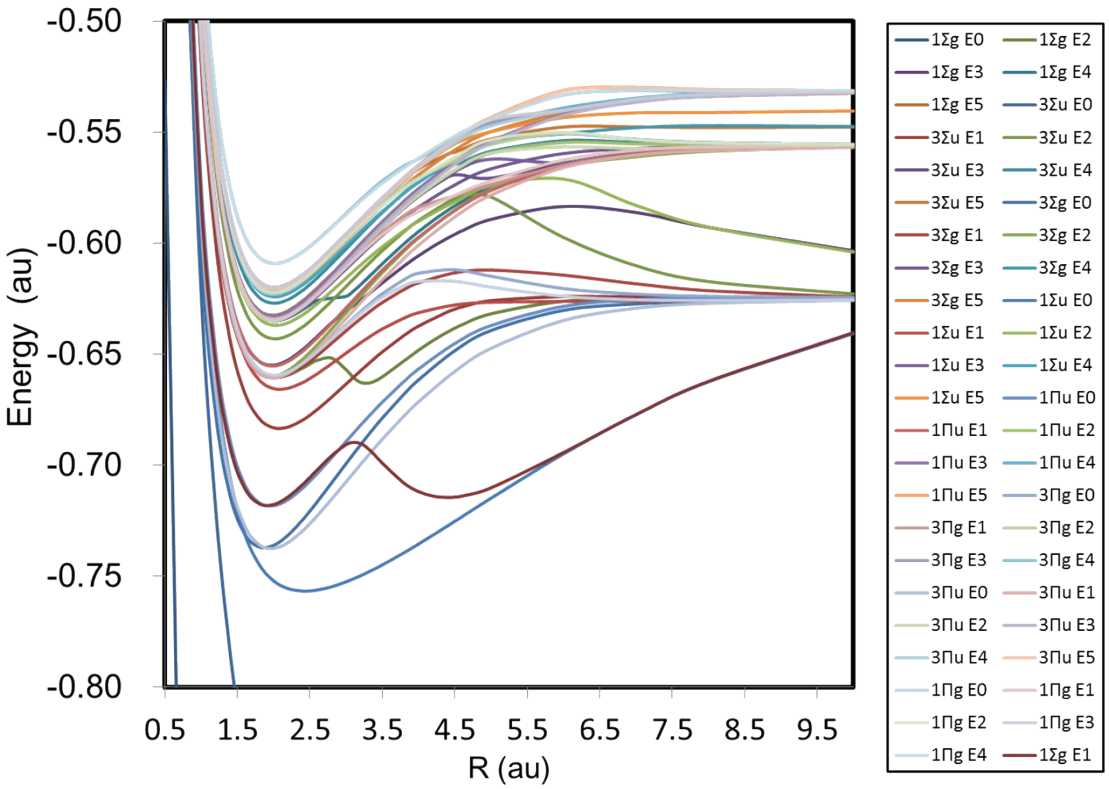


Fig S1. Potential curves of all the Σ and Π states calculated by the FC method at order $n = 3$.