Supporting information for

The threshold-photoelectron spectrum of SiH_2: experiment and modeling with MCTDH method

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S1 Rovibrational Hamiltonian with Radau coordinates

Radau coordinates for an XY_2 molecule are well known[1,2] and consist of the two stretching-type coordinates R_1 and R_2, and of the bending-type coordinate $\widetilde{\gamma}$. The corresponding rovibrational Hamiltonian is also well known[1,2] and is given below attaching the xyz molecular fixed axis system to the molecule so that its origin coincides with the molecular center of mass, the xz plane containing the three atoms, the x-axis bisecting the usual bending angle γ and pointing towards the X atom, and the z axis pointing towards atom Y_1. Using the Radau bending-type coordinate $z = \cos\widetilde{\gamma}$, instead of $\widetilde{\gamma}$, the exact Hamiltonian H can be expanded as[3]

$$H = H_s + H_b + H_r + V(R_1, R_2, z), \tag{S1}$$

where H_s and H_b are kinetic energy operators for the stretching and bending modes, respectively; H_r is the rotational Hamiltonian; and $V(R_1, R_2, z)$ is the potential energy function. It can be deduced from the potential energy function expressed with the usual stretching and bending coordinates r_1, r_2, γ using the transformations in Eqs. (2.19)–(2.22) of Johnson and Reinhardt.[1] The stretching kinetic energy operator takes the following form

$$H_s = \frac{{P_{R_1}}^2}{2m} + \frac{{P_{R_2}}^2}{2m} \tag{S2}$$

where m is the mass of the Y atom; and P_{R_1} and P_{R_2} are conjugate momenta for R_1 and R_2, respectively. The bending kinetic energy operator is

$$H_b = \frac{1}{2m}\left(\frac{1}{R_1^2} + \frac{1}{R_2^2}\right) P_z(1-z^2)P_z, \tag{S3}$$

where m is defined as for Eq. (S2) and P_z is the conjugate momentum for z. The rotational Hamiltonian is written

$$\begin{aligned} H_r = {} & \frac{1}{2m}\left(\frac{1}{R_1^2} + \frac{1}{R_2^2}\right)\left[\frac{N_x^2}{2(1-z)} + \frac{N_y^2}{4} + \frac{N_z^2}{2(1+z)}\right] \\ & - \frac{1}{4m}\left(\frac{1}{R_1^2} - \frac{1}{R_2^2}\right)\left[N_y\{\sqrt{1-z^2}, P_z\} - \frac{\{N_x, N_z\}}{\sqrt{1-z^2}}\right], \end{aligned} \tag{S4}$$

where m is defined as for Eq. (S2); N_x, N_y, and N_z are the components of the rotational angular momentum in the molecular fixed axis system; and $\{,\}$ is the anticommutator. The volume element to be used for the Hamiltonian in Eq. (S1) is $\mathrm{d}R_1\mathrm{d}R_2\mathrm{d}z\sin\theta\mathrm{d}\theta\mathrm{d}\phi\mathrm{d}\chi$, where χ, θ, ϕ are the usual Eulerian angles parameterizing the orientation of the molecular fixed axis system with respect to the space fixed axis system.

S2 Applying the MCTDH method

S2.1 Operators

The MCTDH method[4,5] is used to solve the vibrational problem for the Hamiltonian in Eq. (S1). The MCTDH wavefunction can be obtained from Eq. (19) of Beck *et al.*[4] and takes the following expression in the case of $f = 3$ degrees of freedom

$$\Psi(Q_1, Q_2, Q_3, t) = \sum_{j_1=1}^{n_1}\sum_{j_2=1}^{n_2}\sum_{j_3=1}^{n_3} A_{j_1j_2j_3}(t)\,\phi_{j_1}^{(1)}(Q_1, t)\,\phi_{j_2}^{(2)}(Q_2, t)\,\phi_{j_3}^{(3)}(Q_3, t), \tag{S5}$$

where the nuclear coordinates Q_1, Q_2, and Q_3 correspond respectively to the Radau bond lengths R_1 and R_2, and to the Radau bending coordinate z, the $A_{j_1j_2j_3}$ denote the expansion coefficients;

and $\phi^{(\kappa)}_{j_\kappa}(Q_\kappa, t)$, with $1 \leq \kappa \leq 3$, are the single-particle functions. The single-particle operators $h^{(\kappa)}$, as defined in Eq. (42) of Beck *et al.,*[4] are chosen in the following way:

$$\begin{aligned} h^{(1)} &= \frac{{P_{R_1}}^2}{2m} + V^{(1)}(R_1), \\ h^{(2)} &= \frac{{P_{R_2}}^2}{2m} + V^{(2)}(R_2), \\ h^{(3)} &= \frac{1}{mR_e^2} P_z(1 - z^2)P_z + V^{(3)}(z), \end{aligned} \tag{S6}$$

where R_e is a constant equal to the equilibrium value of either Radau bond length. With the choice indicated by these equations, the residual Hamiltonian H_R, also defined in Eq. (42) of Beck *et al.,*[4] is written

$$H_R = \sum_{i=1}^{2} \frac{1}{2m} \left(\frac{1}{R_i^2} - \frac{1}{R_e^2} \right) P_z(1 - z^2)P_z + \widetilde{V}(R_1, R_2, z), \tag{S7}$$

where the first two terms are expressed as products of two single-particle operators and the potential energy term $\widetilde{V}(R_1, R_2, z)$ is $V(R_1, R_2, z) - V^{(1)}(R_1) - V^{(2)}(R_2) - V^{(3)}(z)$.

S2.2 Overall rotation

Taking into account the overall rotation, in agreement with Eqs. (3)–(5) of the paper, requires rewriting the single-particle operators $h^{(3)}$ in the third of Eqs. (S6) as follows

$$h^{(3)} = \frac{1}{mR_e^2} \left[P_z(1 - z^2)P_z + \frac{V_+}{2(1 + z)} + \frac{V_-}{2(1 - z)} + V_0 \right] + V^{(3)}(z), \tag{S8}$$

while the first and second terms of the residual Hamiltonian H_R in Eq. (S7) should be rewritten

$$\frac{1}{2m} \left(\frac{1}{R_i^2} - \frac{1}{R_e^2} \right) \left[P_z(1 - z^2)P_z + \frac{V_+}{2(1 + z)} + \frac{V_-}{2(1 - z)} + V_0 \right], \tag{S9}$$

where $i = 1$ and 2. In these equations, V_+, V_-, and V_0 are defined in Eqs. (5) of the paper.

S2.3 Basis set functions

The single-particle functions are expanded in the following way

$$\phi^{(\kappa)}_j(Q_\kappa, t) = \sum_{\alpha=1}^{N_\kappa} c^{(\kappa)}_{j\alpha}(t)\, \chi^{(\kappa)}_\alpha(Q_\kappa) \tag{S10}$$

where $1 \leq \kappa \leq 3$; $c^{(\kappa)}_{j\alpha}(t)$ are N_κ time dependent expansion coefficients; and $\chi^{(\kappa)}_\alpha(Q_\kappa)$ are N_κ basis set functions.

For the two stretching modes, the single-particle functions are expanded using for the $\chi^{(\kappa)}_\alpha$ functions, with $\kappa = 1$ and 2, the DVR functions associated with the generalized Gauss-Laguerre quadrature,[6] corresponding to the weight function $x^\rho \exp(-x)$, where $x = \xi R$. The matrix elements between two DVR functions of the stretching operators $1/R^2$ and ${P_R}^2$, appearing in Eqs. (S2)–(S4), can be determined from those computed exactly in Gutlé and Coudert[3] with the Sturmian functions[7]

$$u^{\rho,\xi}_n(R) = N^{\rho,\xi}_n\, x^{\rho/2}\, \exp(-x/2) L^{(\rho)}_n(x), \tag{S11}$$

where $n \geq 0$ is an integer; $N^{\rho,\xi}_n$ is a normalization factor; and $L^{(\rho)}_n(x)$ is a generalized Laguerre polynomial.[8] These functions are an orthonormal basis set because the generalized Laguerre polynomials are orthogonal with respect to integration over the $[0, +\infty)$ range with the weight function.

For the bending coordinate, the single-particle function $\phi^{(3)}_{j_3}(Q_3, t)$ is expanded using for the $\chi^{(3)}_\alpha$ functions the DVR functions associated with the Gauss-Jacobi quadrature, corresponding to the weight function $(1-z)^\gamma(1+z)^\delta$. The matrix elements between two DVR functions of bending operators such as $1/(1+z)$, $1/(1-z)$, $\{\sqrt{1-z^2}, P_z\}$, and $P_z(1-z^2)P_z$, appearing in Eqs. (S3) and (S4), can be obtained from those computed exactly in Gutlé and Coudert[3] with the following functions[9–11]

$$v^{\gamma,\delta}_m(z) = N^{\gamma\delta}_m(1-z)^{\gamma/2}(1+z)^{\delta/2}P^{(\gamma,\delta)}_m(z), \tag{S12}$$

where $m \geq 0$ is an integer; $N^{\gamma,\delta}_m$ is a normalization factor; and $P^{(\gamma,\delta)}_m(z)$ is a Jacobi polynomial.[8] These functions are an orthonormal basis set because the Jacobi polynomials are orthogonal with respect to integration over the $[-1, +1]$ range with the weight function. These functions also are eigenfunctions of the operator

$$P_z(1-z^2)P_z + \frac{1}{2}\left(\frac{\gamma^2}{1-z} + \frac{\delta^2}{1+z}\right), \tag{S13}$$

with eigenvalues $(m+\delta^+)(m+1+\delta^+)$, where $\delta^+ = (\gamma+\delta)/2$.

S2.4 Symmetry relations

The MCTDH wavefunction in Eq. (S5) involves the expansion coefficients A_J depending on the compound index $J = (j_1, j_2, j_3)$ with $1 \leq j_1 \leq n_1$, $1 \leq j_2 \leq n_2$, and $1 \leq j_3 \leq n_3$. Assuming that the symmetry relations in Eqs. (2) of the paper are fulfilled, the n^2n_3 compound indexes are mapped onto the $[1,\ n^2n_3]$ integer interval using an integer function $g(J)$ such that

$$\begin{aligned} &1 \leq g(J) \leq N_s && \text{when} \quad j_1 \leq j_2, \\ &N_s + 1 \leq g(J) \leq N_s + N_a && \text{when} \quad j_1 > j_2, \end{aligned} \tag{S14}$$

where $N_s = n(n+1)n_3/2$ and $N_a = n(n-1)n_3/2$ are the number of indexes with $j_1 \leq j_2$ and $j_1 > j_2$, respectively. The following $n^2n_3 \times n^2n_3$ unitary matrix $U_{J',J}$ is introduced and has the following non-vanishing matrix elements

$$U_{J',J} = \begin{cases} \delta_{j'_1,j_1}\delta_{j'_2,j_2}\delta_{j'_3,j_3} & \text{when} \quad j_1 = j_2, \\ (\delta_{j'_1,j_1}\delta_{j'_2,j_2}\delta_{j'_3,j_3} + \delta_{j'_2,j_1}\delta_{j'_1,j_2}\delta_{j'_3,j_3})/\sqrt{2} & \text{when} \quad j_1 < j_2, \\ (\delta_{j'_1,j_1}\delta_{j'_2,j_2}\delta_{j'_3,j_3} - \delta_{j'_2,j_1}\delta_{j'_1,j_2}\delta_{j'_3,j_3})/\sqrt{2} & \text{when} \quad j_1 > j_2. \end{cases} \tag{S15}$$

Using the unitary matrix U, the matrix $\mathscr{H}$ of the Hamiltonian H is transformed as follows

$$\mathscr{H}'_{J,J'} = \sum_{L,L'} (U^{-1})_{J,L}\mathscr{H}_{L,L'}U_{L',J'} = \sum_{L,L'} U_{L,J}\mathscr{H}_{L,L'}U_{L',J'} \tag{S16}$$

The transformed matrix $\mathscr{H}'_{J,J'}$ is nonzero only if $1 \leq g(J), g(J') \leq N_s$ and $N_s+1 \leq g(J), g(J') \leq N_s + N_a$ because H is invariant under the interchange of atoms Y_1 and Y_2. This implies that the $n^2n_3 \times n^2n_3$ matrix $\mathscr{H}$ is block diagonalized into two blocks. The first $N_s \times N_s$ block is denoted $\mathscr{H}^s$; the second $N_a \times N_a$ block is denoted $\mathscr{H}^a$. These results are also valid for the residual Hamiltonian H_R in Eq. (42) of Beck *al.*[4]

The unitary matrix U can also be used to transform the expansion coefficients A_J. In the case of the upper (lower) sign for the third of Eqs. (2) of the paper, evaluating $\sum_L (U^{-1})_{J,L}A_L$ yields an expansion vector A^s (A^a) with only N_s (N_a) nonvanishing components. Since the unitary matrix is time independent, Eqs. (40) and (43) of Beck *al.*[4] should be replaced by the two equations

$$i\dot{A}^s_J = \sum_L \mathscr{H}^s_{J,L}A^s_L \quad \text{and} \quad i\dot{A}^a_J = \sum_L \mathscr{H}^a_{J,L}A^a_L \tag{S17}$$

involving smaller matrices and vectors. When computing eigenvalues and eigenvectors by energy relaxation,[12] the matrix to be diagonalized in Eq. (80) of this reference should be replaced by either $\mathscr{H}^s$ of $\mathscr{H}^a$ which allows us to assign the appropriate symmetry label to the energy levels.

Using the third of Eqs. (2) of the paper, it can be shown that the projectors, the mean-fields operators, and the density matrices defined respectively in Eqs. (24), (26), and (27) of Beck *al.*[4] fulfill the following relations

$$P^{(1)} = P^{(2)}, \;\; \langle \mathbf{H} \rangle^{(1)} = \langle \mathbf{H} \rangle^{(2)}, \;\; \text{and} \;\; \boldsymbol{\rho}^{(1)} = \boldsymbol{\rho}^{(2)} \tag{S18}$$

These relations imply that the equations of motions for $\boldsymbol{\phi}^{(1)}$ and $\boldsymbol{\phi}^{(2)}$ are identical which is consistent with the second of Eqs. (2) of the paper.

S3 RT Hamiltonian

For a doubly degenerate Λ electronic state split into two electronic states, denoted a and b, by the RT coupling, the Hamiltonian in the adiabatic representation can be expressed as a 2×2 matrix written using as basis set functions the electronic wavefunctions $|a\rangle$ and $|b\rangle$. In agreement with Eqs. (12), (13) and (33) of Jungen and Merer[13] and Eq. (5) of Zhang *et al.*,[14] this matrix is the following:

$$H = \begin{pmatrix} H_a & 0 \\ 0 & H_b \end{pmatrix} + \begin{pmatrix} H_{aa} & H_{ab} \\ H_{ba} & H_{bb} \end{pmatrix} \tag{S19}$$

where H_a and H_b are the vibrational Hamiltonian for the a and b electronic states, respectively, to be obtained from Eq. (S1) where the potential energy function $V(R_1, R_2, z)$ should be replaced by either $V_a(R_1, R_2, z)$ or $V_b(R_1, R_2, z)$ as appropriate; and H_{aa}, H_{bb}, H_{ab}, and H_{ba} are four vibrational operators. They are given by

$$H_{aa} = H_{bb} = \frac{\Lambda^2}{2m} \left(\frac{1}{R_1^2} + \frac{1}{R_2^2} \right) \frac{1}{2(1+z)} \tag{S20}$$

and

$$H_{ab} = H_{ba} = \frac{-K\Lambda}{m} \left(\frac{1}{R_1^2} + \frac{1}{R_2^2} \right) \frac{1}{2(1+z)} + A^{\mathrm{SO}} \Sigma \Lambda. \tag{S21}$$

In Eqs. (S20) and (S21), Λ and Λ^2 are the matrix elements $\langle a|L_z|b\rangle$ and $\langle a|L_z^2|a\rangle$, respectively, where L_z is the component of the electronic angular momentum along the molecule fixed z axis. In Eq. (S21), K is the rotational quantum number introduced in Eq. (3) of the paper; A^{SO} is the spin-orbit coupling constant; and Σ is the quantum number corresponding to S_z the component of the spin operator along the molecule fixed z axis. In the case of the $\widetilde{\mathrm{X}}^+ \, {}^2A_1$ and $\widetilde{\mathrm{A}}^+ \, {}^2B_1$ electronic states of the cation, A^{SO} is 140 cm^{-1} and $\Sigma = \pm 1/2$. The RT wavefunction is written:

$$\Psi(t) = \Psi_a(R_1, R_2, z, t)|a\rangle + \Psi_b(R_1, R_2, z, t)|b\rangle \tag{S22}$$

where $\Psi_a(R_1, R_2, z, t)$ and $\Psi_b(R_1, R_2, z, t)$ are two time dependent vibrational wavefunctions.

When computing the TPE spectrum of the $\Lambda \leftarrow X$ ionization transition, the vibrational function of the X electronic state $\phi(R_1, R_2, z)$ should be time propagated using the rovibronic Hamiltonian in Eq. (S19). The auto-correlation function $c(t)$ should be evaluated taking the initial condition $\Psi_a(R_1, R_2, z, t = 0) = \phi(R_1, R_2, z)/\sqrt{2}$ and $\Psi_b(R_1, R_2, z, t = 0) = \phi(R_1, R_2, z)/\sqrt{2}$. Fourier transforming the auto-correlation function yields the TPS spectra of both the $a \leftarrow X$ and $b \leftarrow X$ ionizing transitions.

S4 Weights used in the TPES modeling

The weights $W_{K,v}$ of a neutral energy level, labeled with the rotational quantum number K and the shorthand vibrational label v, introduced in Section 4, is evaluated taking a rotational temperature

T_{rot} and a vibrational temperature T_{vib}. We have

$$W_{K,v} = g_{K,v} \exp -[(E_{K,v=0} - E_{0,0})/(kT_{\mathrm{rot}}) + (E_{K=0,v} - E_{0,0})/(kT_{\mathrm{vib}})], \tag{S23}$$

where $E_{0,0}$ is the energy $E_{K=0,v=0}$ of the $K = v = 0$ ground level of the neutral and the statistical weight $g_{K,v}$ is

$$g_{K,v} = \sum_{J \geq K} (2J+1) e^{-[J(J+1)\bar{B}]} \tag{S24}$$

where $\bar{B} = (B + C)/2 = 5.3633255 \text{ cm}^{-1}$ is defined in terms of the rotational constants B and C of the neutral.

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Table S3: Potential energy parameters for the neutral triplet $\tilde{a}\,^3B_1$ electronic state

Param.[a]	Value[b]	Param.[a]	Value[b]
r_{12}^{e}	1.464 12(54)	$f_1^{(5)}$	11 498.9(6434)
a_1	1.40[c]	$f_{11}^{(1)}$	3861.8(25356)
$f_0^{(0)}$	−63 672 129.3(89)	$f_{11}^{(2)}$	12 182.9(58050)
$f_{11}^{(0)}$	38 633.9(4713)	$f_{11}^{(3)}$	12 752.4(58127)
$f_{13}^{(0)}$	−1727.4(4608)	$f_{11}^{(4)}$	3279.6(19585)
$f_{111}^{(0)}$	−6386.1(18515)	$f_{13}^{(1)}$	−819.5(28519)
$f_{113}^{(0)}$	−4395.8(14057)	$f_{13}^{(2)}$	4590.4(69633)
$f_{1111}^{(0)}$	−3259.3(90122)	$f_{13}^{(3)}$	6311.6(70929)
$f_{1113}^{(0)}$	−6732.7(64927)	$f_{13}^{(4)}$	3353.4(23973)
$f_{1133}^{(0)}$	−7100.7(84502)	$f_{111}^{(1)}$	−8481.0(99873)
$f_0^{(1)}$	59 251.9(1736)	$f_{111}^{(2)}$	−6821.8(147198)
$f_0^{(2)}$	210 204.0(14475)	$f_{111}^{(3)}$	−510.1(65016)
$f_0^{(3)}$	476 592.1(54063)	$f_{113}^{(1)}$	−12 352.9(78115)
$f_0^{(4)}$	668 490.1(100682)	$f_{113}^{(2)}$	−13 183.3(117352)
$f_0^{(5)}$	534 722.8(98038)	$f_{113}^{(3)}$	−4986.0(52050)
$f_0^{(6)}$	225 611.3(47783)	$f_{1111}^{(1)}$	−13 209.3(345172)
$f_0^{(7)}$	38 693.7(9197)	$f_{1111}^{(2)}$	−7961.8(241989)
$f_1^{(1)}$	15 965.3(5006)	$f_{1113}^{(1)}$	−17 105.4(247970)
$f_1^{(2)}$	53 320.7(18452)	$f_{1113}^{(2)}$	−9957.4(173649)
$f_1^{(3)}$	78 373.8(31615)	$f_{1133}^{(1)}$	−16 781.2(323010)
$f_1^{(4)}$	49 300.2(23825)	$f_{1133}^{(2)}$	−7986.1(226278)

[a] Parameters are defined in Eqs. (1)–(4) of Bunker and Jensen.[15]

[b] In cm^{-1} except for r_{12}^{e} and a_1 which are in Å and Å^{-1}, respectively.

[c] Constrained value.

Table S4: Potential energy parameters for the cation ground $\widetilde{\mathrm{X}}^{+}\,{}^{2}A_1$ and first excited $\widetilde{\mathrm{A}}^{+}\,{}^{2}B_1$ electronic states

Param.[a]	Value[b]	Param.[a]	Value[b]
$r_{12}^{(\mathrm{res})}$	1.4692(33)	$f_{111}^{(1,+)}$	3807.2(450440)
a_1	1.40[c]	$f_{111}^{(2,+)}$	−552.9(288337)
$f_{0}^{(0)}$	−63 606 558.2(603)	$f_{113}^{(1,+)}$	877.6(365305)
$f_{11}^{(0)}$	37 006.9(26397)	$f_{113}^{(2,+)}$	3292.8(245871)
$f_{13}^{(0)}$	−1934.2(31345)	$f_{1111}^{(1,+)}$	3147.2(627633)
$f_{111}^{(0)}$	−2098.9(145003)	$f_{1113}^{(1,+)}$	−5087.8(489254)
$f_{113}^{(0)}$	−2950.8(114029)	$f_{1133}^{(1,+)}$	739.9(654424)
$f_{1111}^{(0)}$	−2496.7(249324)	$f_{0}^{(1,-)}$	−15 974.6(8491)
$f_{1113}^{(0)}$	−631.8(194817)	$f_{0}^{(2,-)}$	−17 407.4(48563)
$f_{1133}^{(0)}$	3372.1(260489)	$f_{0}^{(3,-)}$	−44 687.9(114072)
$f_{0}^{(1,+)}$	45 936.1(9072)	$f_{0}^{(4,-)}$	−36 360.9(113209)
$f_{0}^{(2,+)}$	94 283.0(36646)	$f_{0}^{(5,-)}$	−11 807.7(39611)
$f_{0}^{(3,+)}$	83 474.0(51757)	$f_{1}^{(1,-)}$	4474.8(24638)
$f_{0}^{(4,+)}$	31 000.3(23378)	$f_{1}^{(2,-)}$	2739.2(48851)
$f_{1}^{(1,+)}$	17 188.5(31373)	$f_{1}^{(3,-)}$	3398.6(28094)
$f_{1}^{(2,+)}$	58 170.0(102786)	$f_{11}^{(1,-)}$	−8154.2(62812)
$f_{1}^{(3,+)}$	71 406.8(136858)	$f_{11}^{(2,-)}$	−14 052.2(50297)
$f_{1}^{(4,+)}$	27 443.5(61315)	$f_{13}^{(1,-)}$	−10 887.1(168553)
$f_{11}^{(1,+)}$	−4018.6(135577)	$f_{13}^{(2,-)}$	−22 489.1(277134)
$f_{11}^{(2,+)}$	−4077.6(128642)	$f_{13}^{(3,-)}$	−17 194.4(148501)
$f_{13}^{(1,+)}$	−2750.0(181541)	$f_{111}^{(1,-)}$	12 301.2(82624)
$f_{13}^{(2,+)}$	−6085.8(295486)	$f_{113}^{(1,-)}$	4240.0(239913)
$f_{13}^{(3,+)}$	−5237.9(163396)	$f_{113}^{(2,-)}$	10 848.0(230242)

[a] Parameters are defined in Eqs. (1)–(4) of Gu *et al.*[16] $\sigma = -/+$ for the ground $\widetilde{\mathrm{X}}^{+}\,{}^{2}A_1$ and first excited $\widetilde{\mathrm{A}}^{+}\,{}^{2}B_1$ electronic states, respectively.

[b] In cm^{-1} except for $r_{12}^{(\mathrm{res})}$ and a_1 which are in Å and Å^{-1}, respectively.

[c] Constrained value.

Table S5: Vibrational energies of the ground $\widetilde{\mathrm{X}}\,^1A_1$ electronic state of the neutral calculated in Section 3.2.2 are compared to those from Clark *et al.*[17] Energies are given in cm^{-1} with respect to the ground vibrational state. Vibrational states are assigned with the three vibrational quantum numbers v_1, v_2, v_3 in parentheses, where v_2 is the bent molecule quantum number.

State	Clark *et al.*[17]	*This work*	State	Clark *et al.*[17]	*This work*
(010)	998	998	(011)	2975	2978
(020)	1978	1980	(110)	3002	3002
(001)	1996	1997	(120)	3914	3915
(100)	2009	2009	(101)	3913	3923
(030)	2954	2954	(200)	3930	3932

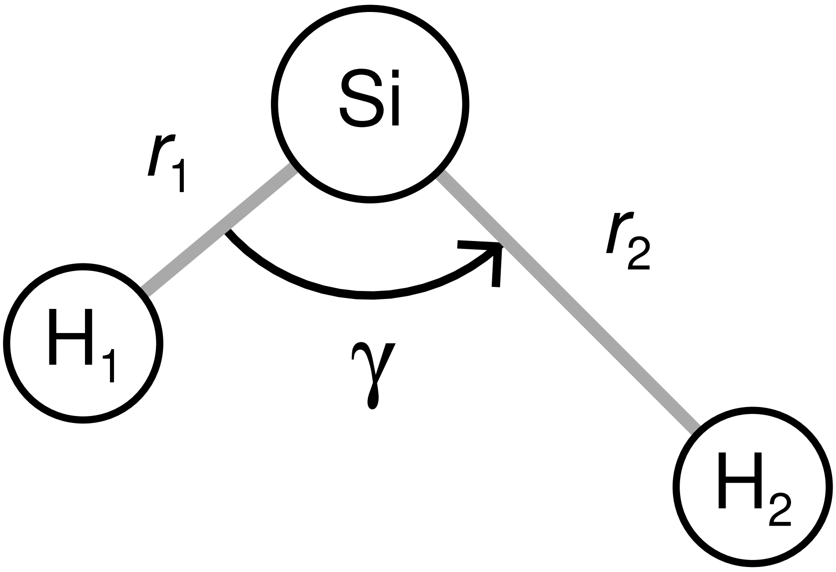

Figure S1: The bond lengths r_1 and r_2 and the bond angle γ are defined.

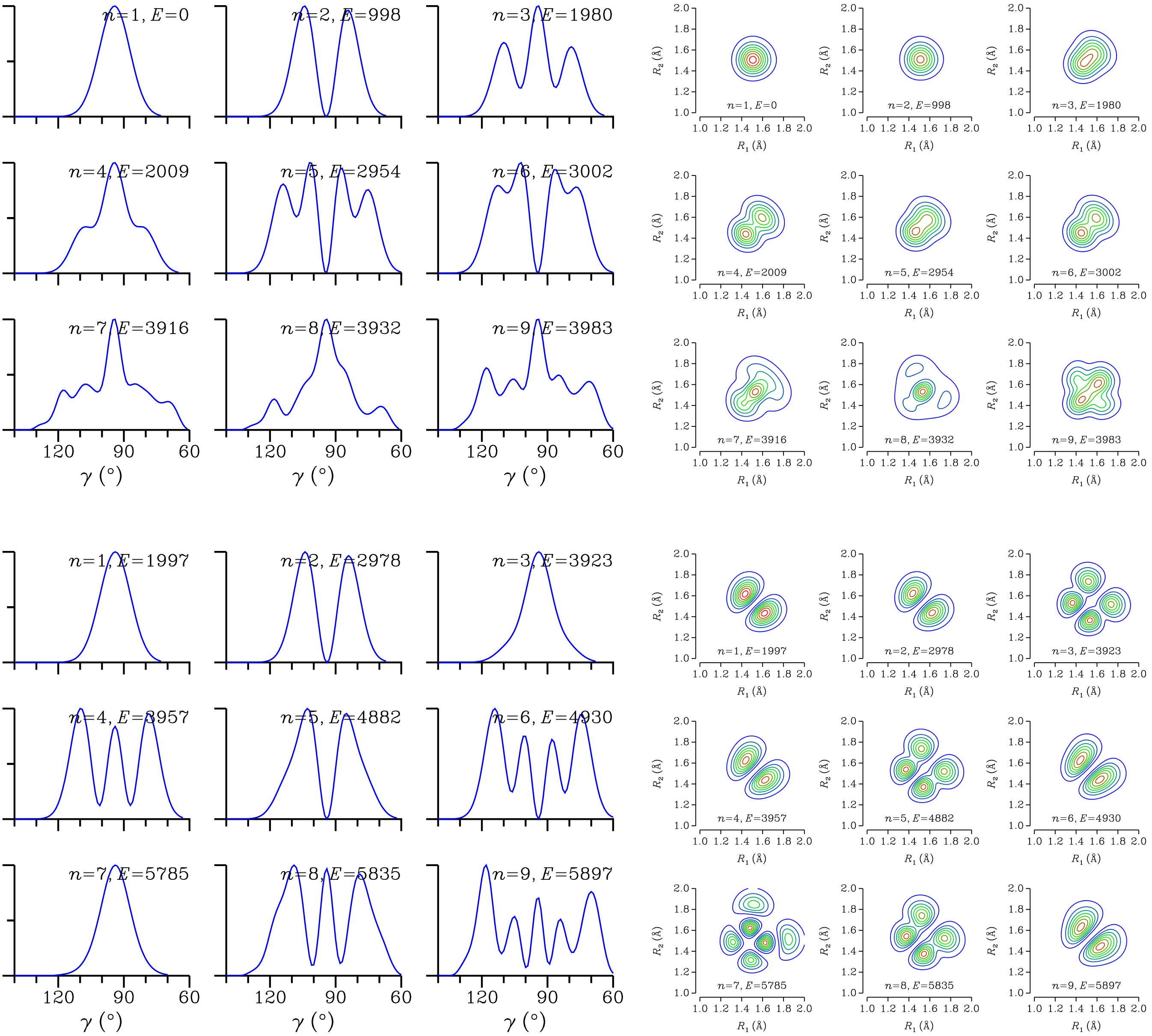

Figure S2: For the 9 lowest symmetrical vibrational states, upper panels, and the 9 lowest antiysymmetrical vibrational states, lower panels, of the ground $\widetilde{\mathrm{X}}\,{}^1A_1$ electronic state of the neutral, the variations of the bending, left panels, and stretching, right panels, probability densities, as defined in Eqs. (7) of the paper, are shown. $p_b(\tilde{\gamma})$ is plotted as a function of the Radau bending angle $\tilde{\gamma}$ in degrees. Contour plots of $p_s(R_1, R_2)$ are drawn with respect to the Radau stretching coordinates R_1 and R_2 in Å. Each vibrational state is identified by a counter n and its vibrational energy in cm^{-1}.

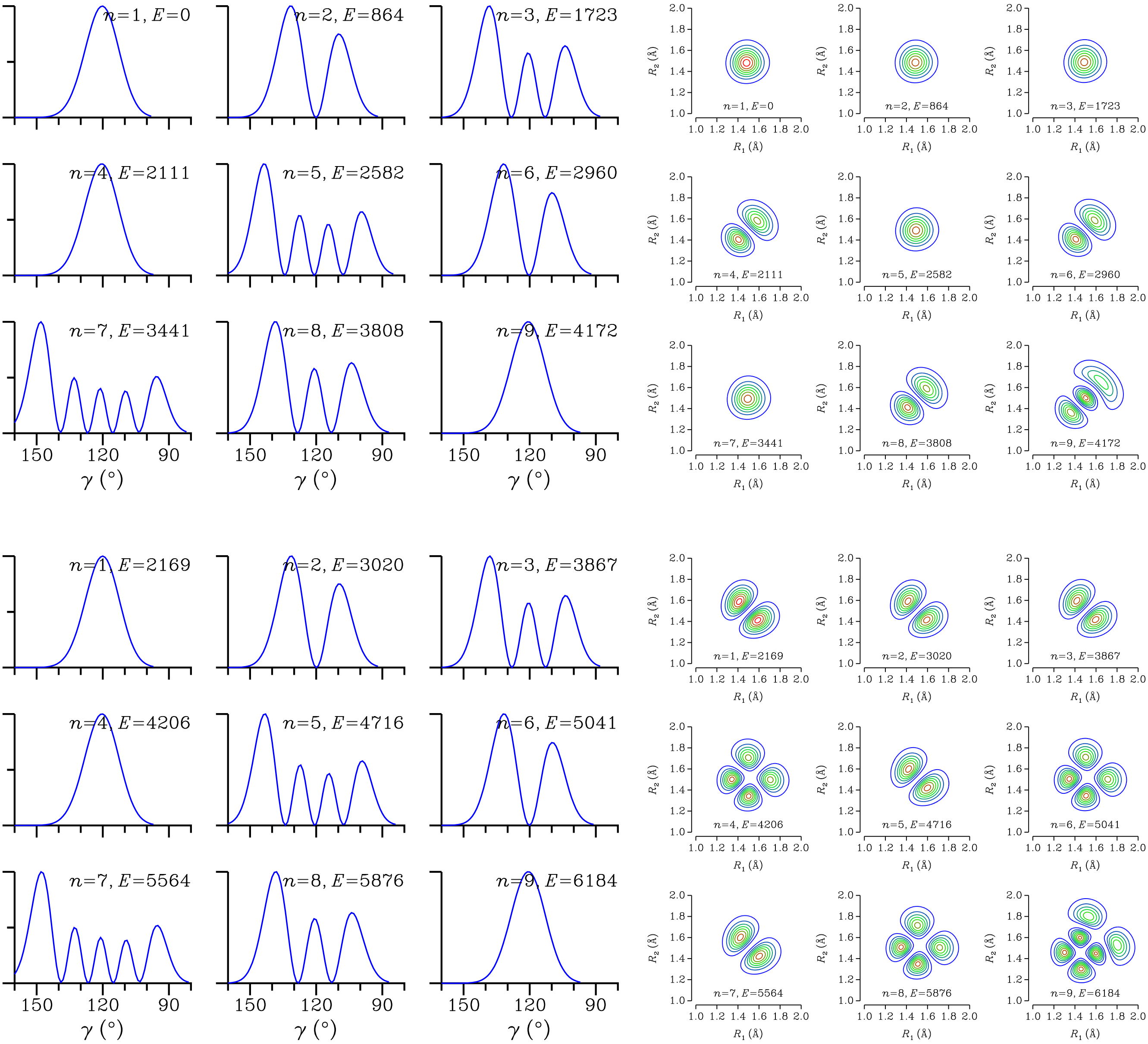

Figure S3: For the 9 lowest symmetrical vibrational states, upper panels, and the 9 lowest antiysymmetrical vibrational states, lower panels, of the triplet ã $^3B_1$ electronic state of the neutral, the variations of the bending, left panels, and stretching, right panels, probability densities, as defined in Eqs. (7) of the paper, are shown. $p_b(\tilde{\gamma})$ is plotted as a function of the Radau bending angle $\tilde{\gamma}$ in degrees. Contour plots of $p_s(R_1, R_2)$ are drawn with respect to the Radau stretching coordinates R_1 and R_2 in Å. Each vibrational state is identified by a counter n and its vibrational energy in cm^{-1}.

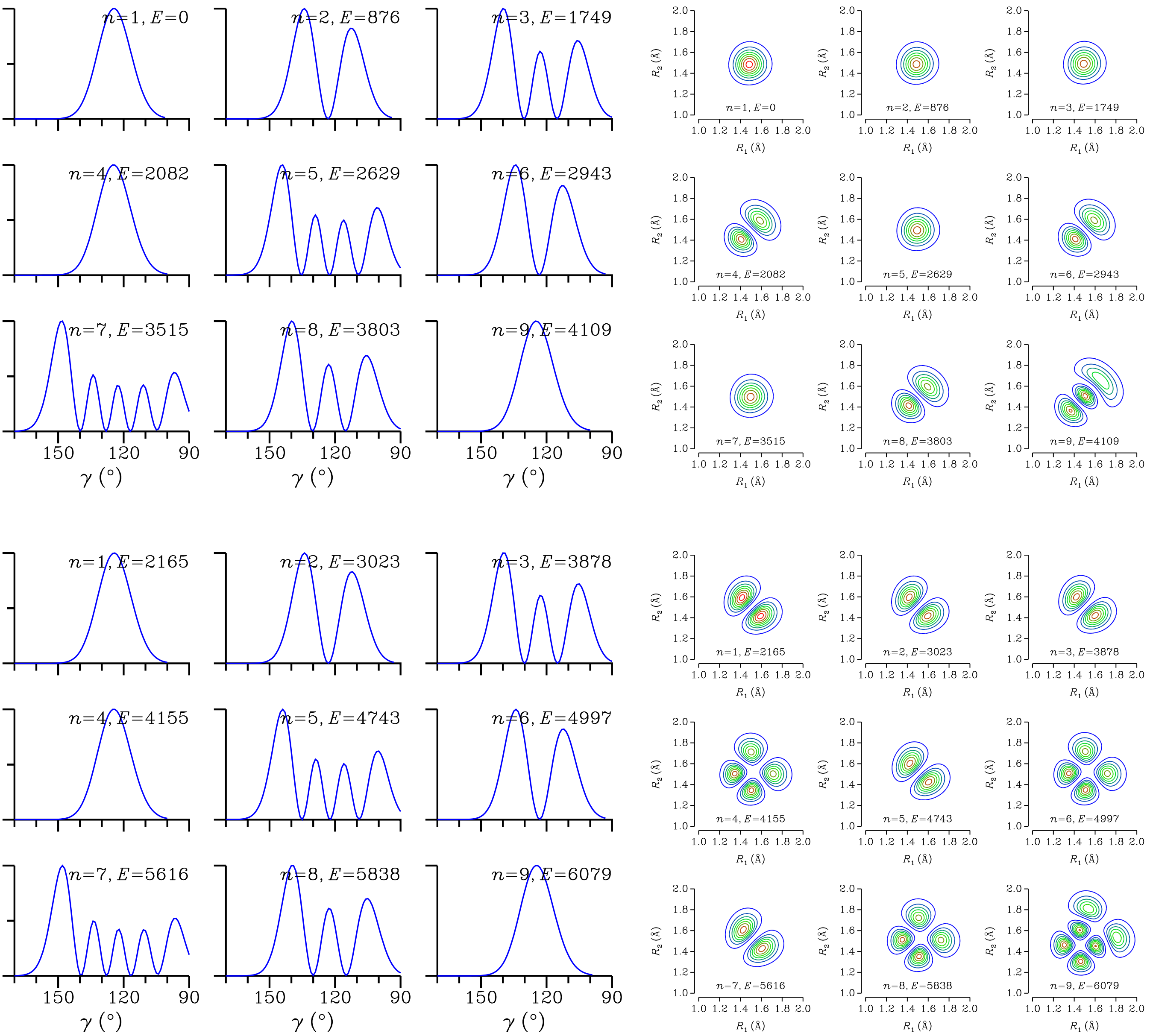

Figure S4: For the 9 lowest symmetrical vibrational states, upper panels, and the 9 lowest antiysymmetrical vibrational states, lower panels, of the ground $\widetilde{\mathrm{X}}^{+}\ {}^{2}A_1$ electronic state of the cation, the variations of the bending, left panels, and stretching, right panels, probability densities, as defined in Eqs. (7) of the paper, are shown. $p_b(\tilde{\gamma})$ is plotted as a function of the Radau bending angle $\tilde{\gamma}$ in degrees. Contour plots of $p_s(R_1, R_2)$ are drawn with respect to the Radau stretching coordinates R_1 and R_2 in Å. Each vibrational state is identified by a counter n and its vibrational energy in cm^{-1}.

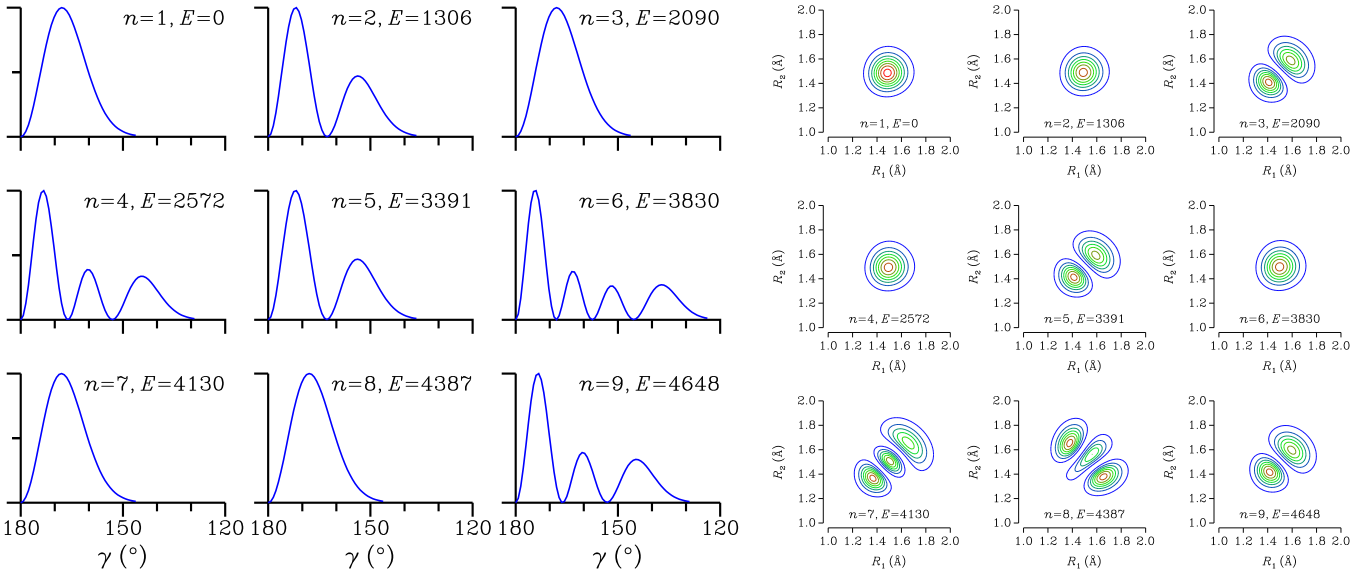

Figure S5: For the 9 lowest symmetrical rovibronic states of the excited $\widetilde{\mathrm{A}}^{+}\,{}^{2}B_1$ electronic state of the cation with $K = 0$, the variations of the bending, left panel, and stretching, right panel, probability densities, as defined in Eqs. (7) of the paper, are shown. $p_b(\tilde{\gamma})$ is plotted as a function of the Radau bending angle $\tilde{\gamma}$ in degrees. Contour plots of $p_s(R_1, R_2)$ are drawn with respect to the Radau stretching coordinates R_1 and R_2 in Å. Each vibrational state is identified by a counter n and its vibrational energy in cm^{-1}.

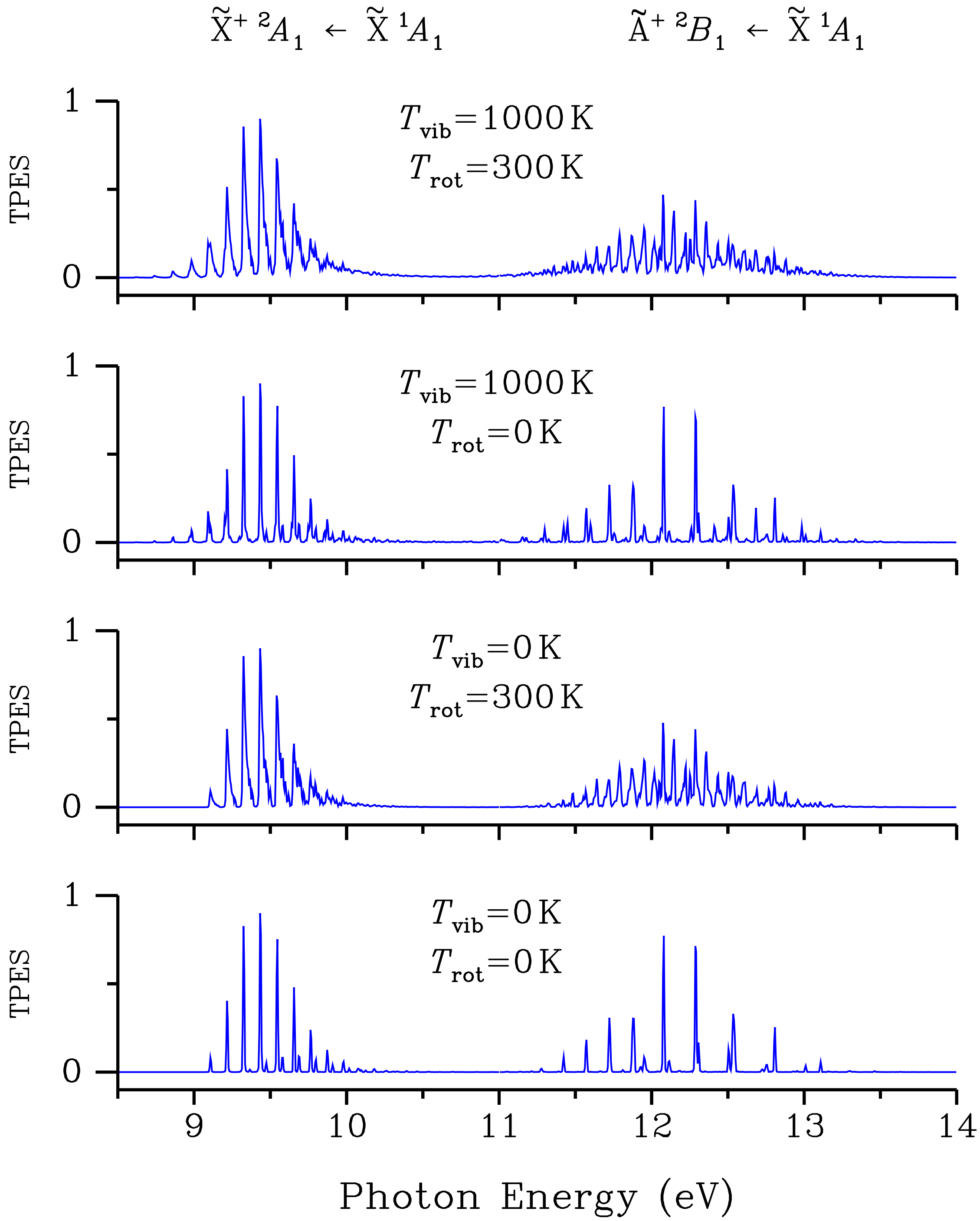

Figure S6: Calculated TPE spectra of the photoionizing transitions originating from the ground $\tilde{X}\,^1A_1$ electronic state of the neutral are plotted as functions of the photon energy in eV. The selection rule $K^+ = K'' \pm 1$ was adopted. Each panel is characterized by a rotational temperature $T_{\rm rot}$ and a vibrational temperature $T_{\rm vib}$ given in Kelvin. The intensity scale of the two transitions differs.

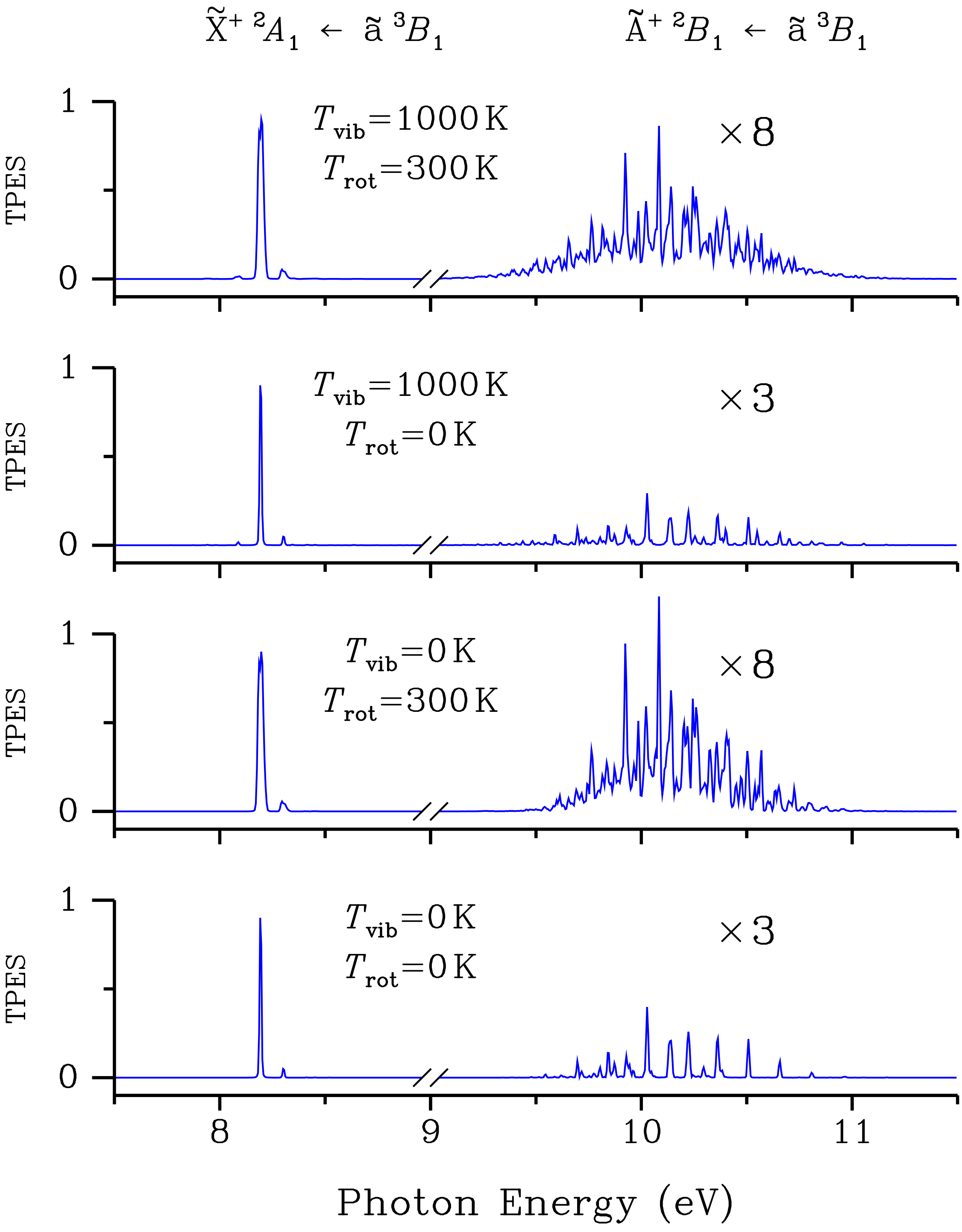

Figure S7: Calculated TPE spectra of the photoionizing transitions originating from the triplet $\tilde{a}\,^3B_1$ electronic state of the neutral are plotted as functions of the photon energy in eV. The selection rule $K^+ = K'' \pm 1$ was adopted. Each panel is characterized by a rotational temperature $T_{\rm rot}$ and a vibrational temperature $T_{\rm vib}$ given in Kelvin. The intensity scale of the two transitions differs.