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

I. THE CHANGE FROM THE SYMMETRY TO THE ATOMIC BASIS

In order to perform the dynamical calculations, some processing of the *ab initio* 15x15 relativistic potential matrix provided by MOLPRO is required. Being labeled by global features like C_{2v} symmetry and total spin, the 15 molecular electronic states do not correlate (for large R) to the internal states of the colliding atoms. A change to a more *dynamical* basis to get potentials and couplings labeled by the asymptotic states of the atoms, and thus suitable to be introduced in the scattering equations, is needed.

Let us recall that the 15 electronic states considered above are labeled by A_1, A_2, B_1 or B_2 (the irreducible representation of the group C_{2v} they belong to) plus S and M_S quantum numbers (total electronic spin and its projection). In addition, these states have a defined value of Λ (the absolute value of the projection of the orbital electronic angular momentum on the internuclear axis, $\Lambda = |M_L|$) [1]. We will name this initial C_{2v}-symmetry basis as B1 and schematically note it as $|\mathrm{Sym}, (L), \Lambda, S, M_S\rangle$, where Sym stands for the irreducible representation; the value of L has been enclosed in parentheses in order to remind that the electronic orbital angular momentum is not strictly a good quantum number, being only asymptotically defined. The list of the 15 states in basis B1, characterized by their labels, can be found in Table I. The spectroscopic notation, including the atomic electrostatic term (^{2S+1}L) they correspond to, is also shown. As noted above, this basis is not convenient for the dynamics: the spin-orbit couplings among these electronic states do not vanish at infinity, where interaction between fragments should disappear, as they do not correlate to particular internal states of the colliding atoms. Moreover, the couplings are in general complex numbers and this complicates their use.

N	Spectroscopic notation	$\|Sym, (L), \Lambda, S, M_S\rangle$
1	$^1\Sigma^+(^1D)$	$\|A_1, (2), 0, 0, 0\rangle$
2	$^1\Delta(^1D)$	$\|A_1, (2), 2, 0, 0\rangle$
3	$^1\Sigma^+(^1S)$	$\|A_1, (0), 0, 0, 0\rangle$
4	$^1\Pi(^1D)$	$\|B_1, (2), 1, 0, 0\rangle$
5	$^3\Pi(^3P)$	$\|B_1, (1), 1, 1, +1\rangle$
6	$^3\Pi(^3P)$	$\|B_1, (1), 1, 1, 0\rangle$
7	$^3\Pi(^3P)$	$\|B_1, (1), 1, 1, -1\rangle$
8	$^1\Pi(^1D)$	$\|B_2, (2), 1, 0, 0\rangle$
9	$^3\Pi(^3P)$	$\|B_2, (1), 1, 1, +1\rangle$
10	$^3\Pi(^3P)$	$\|B_2, (1), 1, 1, 0\rangle$
11	$^3\Pi(^3P)$	$\|B_2, (1), 1, 1, -1\rangle$
12	$^1\Delta(^1D)$	$\|A_2, (2), 2, 0, 0\rangle$
13	$^3\Sigma^-(^3P)$	$\|A_2, (1), 0, 1, +1\rangle$
14	$^3\Sigma^-(^3P)$	$\|A_2, (1), 0, 1, 0\rangle$
15	$^3\Sigma^-(^3P)$	$\|A_2, (1), 0, 1, -1\rangle$

TABLE SI. Electronic states in C_{2v}-symmetry basis, B1, numbered from 1 to 15.

The atomic states which can be experimentally prepared correspond to the spectral terms, named $^{2S+1}L_j$ and labeled by L, S and j (total electronic angular momentum) quantum numbers. Ω, the projection of j onto an axis, could be also selected in principle (J and M_J are used in the literature instead of the symbols j and Ω which we prefer here). In what follows, our aim is to change from basis B1 to a basis which correlates to these atomic states. We may conceptually decompose the process of changing basis into two steps: i) first we can change from the current C_{2v}-symmetry basis to a definite signed-M_L basis, $|(L), M_L, S, M_S\rangle$, which we will name as basis B2; ii) from the latter we will change to a third basis, basis B3, noted as $|(L, S)j, \Omega\rangle$ (with $\Omega = M_L + M_S$), which at infinity diagonalizes the electronic Hamiltonian of each atom, thus correlating to the spectral terms $^{2S+1}L_j$. We will examine each step separately below.

The first change of basis is equivalent to the one which relates the real spherical harmonics (of defined C_{2v}-symmetry) to the complex spherical harmonics (of defined spherical symmetry). For example, states (4) and (8) in basis B1, with $\Lambda = 1$ (Π states), are transformed using the same expressions which, for hydrogenic atoms, relate ψ_{px}, ψ_{py} orbitals with $\psi_{p_{+1}}$, $\psi_{p_{-1}}$ orbitals. The list of quantum numbers of this second basis, B2, is given in Table II, together with the equations for the change of basis. In addition to performing these linear combinations, which change to a signed-M_L basis, some states of basis B1 are simply multiplied by the imaginary unit (i). This way we are able to get a matrix which is real numbered at every R. An additional advantage of basis B2 is that the number of couplings is reduced to a minimum as only states with the same value of $\Omega = M_L + M_S$ are coupled.

N	$\|(L), M_L, S, M_S\rangle$	Change
I	$\|0, 0, 0, 0\rangle$	$(I) = (3)$
II	$\|2, +2, 0, 0\rangle$	$(II) = \frac{1}{\sqrt{2}}((2) + i(12))$
III	$\|2, +1, 0, 0\rangle$	$(III) = -\frac{1}{\sqrt{2}}((4) + i(8))$
IV	$\|2, 0, 0, 0\rangle$	$(IV) = 1$
V	$\|2, -1, 0, 0\rangle$	$(V) = \frac{1}{\sqrt{2}}((4) - i(8))$
VI	$\|2, -2, 0, 0\rangle$	$(VI) = \frac{1}{\sqrt{2}}((2) - i(12))$
VII	$\|1, +1, 1, +1\rangle$	$(VII) = -\frac{1}{\sqrt{2}}((5) + i(9))$
VIII	$\|1, +1, 1, 0\rangle$	$(VIII) = -\frac{1}{\sqrt{2}}((6) + i(10))$
IX	$\|1, +1, 1, -1\rangle$	$(IX) = -\frac{1}{\sqrt{2}}((7) + i(11))$
X	$\|1, 0, 1, +1\rangle$	$(X) = i(13)$
XI	$\|1, 0, 1, 0\rangle$	$(XI) = i(14)$
XII	$\|1, 0, 1, -1\rangle$	$(XII) = i(15)$
XIII	$\|1, -1, 1, +1\rangle$	$(XIII) = \frac{1}{\sqrt{2}}((5) - i(9))$
XIV	$\|1, -1, 1, 0\rangle$	$(XIV) = \frac{1}{\sqrt{2}}((6) - i(10))$
XV	$\|1, -1, 1, -1\rangle$	$(XV) = \frac{1}{\sqrt{2}}((7) - i(11))$

TABLE SII. Electronic states in signed-M_L basis, B2, numbered using roman numerals, and their relation with the states of basis B1, given in ordinary numerals.

The second step involves diagonalizing the potential matrix expressed in basis B2 at infinity, $V_{B2}(R = \infty)$ to obtain a diagonal matrix V_d. Let us name as C the corresponding change of basis: $V_d = C^{-1} \cdot V_{B2}(R = \infty) \cdot C$. Only states in B2 with the same Ω are coupled and hence each Ω box can be diagonalized independently. Each eigenvalue should correspond to a spectral term, $S(^{2S+1}L_j)$, with a particular projection Ω, and the energy gaps between them should reproduce the experimental gaps. Now, by applying to B2 at every R the *same* change of basis, C, we get a third basis, B3, and the corresponding potential matrix, $V_{B3}(R) = C^{-1} \cdot V_{B2}(R) \cdot C$. The list of B3 vectors and their quantum numbers are given in Table III. Electronic basis B3 is the one we will consider for the dynamics: it is related to B1 by the same change of basis at all distances, and each electronic state (and the associated potential diagonal terms) correlates to particular internal states of the incoming atoms, the couplings between them vanishing at long distances.

N	Asymptotic correlation	$\vert(L,S)j,\Omega\rangle$
1	$^3P_2(\Omega = 0)$	$\vert(1,1)2,0\rangle$
2	$^3P_2(\Omega = +2)$	$\vert(1,1)2,+2\rangle$
3	$^3P_2(\Omega = +1)$	$\vert(1,1)2,+1\rangle$
4	$^3P_1(\Omega = 0)$	$\vert(1,1)1,0\rangle$
5	$^3P_2(\Omega = -1)$	$\vert(1,1)2,-1\rangle$
6	$^3P_2(\Omega = -2)$	$\vert(1,1)2,-2\rangle$
7	$^1D_2(\Omega = +2)$	$\vert(2,0)2,+2\rangle$
8	$^3P_1(\Omega = +1)$	$\vert(1,1)1,+1\rangle$
9	$^3P_0(\Omega = 0)$	$\vert(1,1)0,0\rangle$
10	$^1D_2(\Omega = +1)$	$\vert(2,0)2,+1\rangle$
11	$^1D_2(\Omega = 0)$	$\vert(2,0)2,0\rangle$
12	$^3P_1(\Omega = -1)$	$\vert(1,1)1,-1\rangle$
13	$^1S_0(\Omega = 0)$	$\vert(0,0)0,0\rangle$
14	$^1D_2(\Omega = -1)$	$\vert(2,0)2,-1\rangle$
15	$^1D_2(\Omega = -2)$	$\vert(2,0)2,-2\rangle$

TABLE SIII. Electronic states in basis B3, numbered from 1 to 15; the atomic states of S to which they correlate are given in the first column.

The way used to define B2 is somewhat arbitrary: if we changed the phase of any vector in B2, by simply multiplying by (-1) one of the linear combinations in Table II, the matrix of the potential $V_{B2}(R)$ would still be real and eigenstates with defined M_L would still be obtained. The definition of B3 is also arbitrary: the eigenstates of the potential are obtained by numerical diagonalization and their relative phases are thus random. There exist conventions to solve analogous arbitrariness, and fix the relative phases of different eigenstates of the projection of an angular momentum. Indeed, we do need states to satisfy particular phase-relations among them: this will be required for Eq. (4) (see the main text) to be valid in order to get channels with defined l (relative angular momentum) in the space-fixed system, when solving the scattering equations. Such a change of basis is commonly used in the closely related problem of the collision of an atom with a rigid rotor: channels in the body-fixed (BF) system with defined quantum numbers j and Ω are combined using Eq. (4) in order to get channels in the SF system with defined l and thus parity; different parities are decoupled. However, Eq. (4) is based on the conventions of the spherical harmonics. To make sure that such conventions are valid for the electronic atomic basis we consider, a heuristic procedure is applied here. Before entering into details, let us recall two statements. The first one is that the matrix elements of the potential matrix in basis B2 at infinity (where L is defined) are related through the Wigner-Eckart theorem, which can be applied separately to S and L angular momenta. However, for the Wigner-Eckart relations to be valid, the electronic states have to keep a particular phase-relation. The second statement is that the change of basis which diagonalizes the spin-orbit perturbation within a ^{2S+1}L atomic term, if the small couplings with other atomic terms are neglected, is given by Clebsch-Gordan coefficients. Again, this imposes a particular phase-relation to the electronic states in B3. Based in these two statements, we have implemented a two-step heuristic procedure in order to fix the phase of the electronic states. First we check if the Wigner-Eckart relations among the matrix elements in basis B2 are are consistent in sign. If needed, particular electronic states are changed sign for Wigner-Eckart relations to be fulfilled. In our case, changing the sign of states V, IX, X and XV was necessary and we applied such additional change to the definition of basis B2 just before diagonalizing [2]. In a second step, we compare the numerical eigenvectors which diagonalize V_{B2} at infinity with the corresponding approximate eigenvectors in terms of Clebsch-Gordan coefficients; as expected, they are found very similar, except for the small contribution of states belonging to other atomic terms. In a few cases, both eigenvectors differ in a global sign, and we proceed to change the sign of that particular numerical eigenvector. We have checked that this procedure in two steps is satisfactory enough in order to get potential matrices which do not connect scattering channels of different parities when changed to SF basis.

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[1] The correspondence between irreducible representations of $C_{\infty v}$ and C_{2v} allows to assign Λ and ± (behavior under reflection symmetry, for Σ states) labels.

[2] Accordingly, the linear combinations corresponding to states V, IX, X and XV in Table II should be changed sign.