

COLLISIONS OF OH AND OTHER ORBITALLY DEGENERATE MOLECULES: A CONSISTENT TREATMENT OF THE AZIMUTHAL DEPENDENCE OF THE INTERACTION POTENTIAL

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Received 17 September 1985

The description of the interaction potential in collisions involving one or both partners with orbital degeneracy is shown to depend on the choice of phase for the azimuthal dependence of the electronic wavefunctions describing the molecular states of the partners. This has important consequences in the interpretation of $\text{OH}(X^2\Pi)$ collisions, especially in regard to mechanisms for Λ -doublet population inversion. Theory and experiment are brought into accord for $\text{OH} + \text{H}_2$ collisions.

1. Introduction

There has been a tortuous history concerning the phase conventions for linear molecules in orbitally degenerate states [1–13]. Recently an excellent review by Alexander and Dagdigian [14] has clarified the relationship between the sign conventions for the basis functions in both Hund's case (a) and case (b) coupling and the physical orientation of the electron charge distribution with respect to the total angular momentum vector J of the molecule [5–7]. However, ambiguities still remain in the treatment of collisions involving orbitally degenerate species because the matrix elements of the interaction potential depend on the phase convention adopted for the electronic wavefunctions of the separated partners.

In the scattering process the interaction potential relates to fixed nuclear configurations in which in general there are no orbital degeneracies because the axial symmetry is broken. For example, in an atom-diatom collision there exists only a plane of symmetry and the electronic states are either A' or A'' in the C_s point group. Thus the interaction potential, being the expect-

ation value of the electronic Hamiltonian over the electronic coordinates, is diagonal and *real*. However, when using the products of the wavefunctions of the unperturbed collision partners as a basis, it is necessary to define the parities of the wavefunctions of the separate partners. When one or both collision partners are orbitally degenerate this causes the basis functions to be *complex*, and the interaction potential therefore has off-diagonal matrix elements whose values depend on the phase convention chosen. Before and after the collision the parity of each partner is well defined; during the collision the parity of each partner is lost through the lowering of the symmetry (although of course the overall parity of the system is conserved). For a given $J_i \rightarrow J_f$ energy transfer event in one partner, the cross sections for $(+) \rightarrow (+)$ parity levels need not equal that for $(-) \rightarrow (-)$; nor that for $(+) \rightarrow (-)$ equal that for $(-) \rightarrow (+)$ [2,6,7,15]. This has the consequence that collisions may cause the Λ -doublets of such a partner to become unequally populated.

In this Letter we discuss how to ensure consistency in defining the matrix elements of the interaction potential, leading to energy transfer cross sections that

are independent of phase conventions, as they must be. We were prompted to examine this problem when it became apparent that the elegant experimental results on $\text{OH}(X^2\Pi) + \text{H}_2(X^1\Sigma_g^+)$ scattering obtained by Andresen, Häusler and Lülf [16] are at variance with earlier theoretical predictions [17–20]. Re-examination discloses inconsistencies in some previous theoretical treatments. In some cases these errors have arisen from an incorrect formulation of the molecular wavefunctions [13], or have been wrongly attributed to incorrect assignment of the Λ -doublets [16]. If the critique of ref. [16] were correct, which it is not, it would raise serious doubts about the interpretation of the unequal Λ -doublet populations observed, for example, in the photodissociation of H_2O [21] and HONO [22].

2. Matrix elements of the interaction potential

The wavefunction for a $2S+1\Lambda$ state, with $\Lambda \neq 0$ and well defined parity under inversion of the space-fixed coordinates, may be written in the case (a) basis set as:

$$|n\Lambda\Sigma JM\Omega \pm\rangle = 2^{-1/2} [|n\Lambda\Sigma\rangle |JM\Omega\rangle \pm (-1)^{J-S} |n-\Lambda S-\Sigma\rangle |JM-\Omega\rangle], \quad (1)$$

where the \pm sign denotes the inversion parity (see below). Levels with parity $(-1)^J$ for an even number of electrons, and $(-1)^{J-1/2}$ for an odd number of electrons, are designated e levels; whereas f levels have the correspondingly opposite parity [23,24]. Here $|n\Lambda\Sigma\rangle$ is the electronic wavefunction, and $|JM\Omega\rangle$ is the rotational wavefunction which has the form

$$|JM\Omega\rangle = [(2J+1)/8\pi^2]^{1/2} D_{M\Omega}^J(\alpha\beta\gamma)^*, \quad (2)$$

where $D_{M\Omega}^J$ is a Wigner rotation matrix element and $(\alpha\beta\gamma)$ are the Euler angles that relate by an active rotation [10] the space-fixed frame (XYZ) to the molecule-fixed frame (xyz).

In the molecule-fixed frame the z -axis lies along the internuclear axis but the orientations of x and y are arbitrary corresponding to the chosen value of the redundant Euler angle γ . Two conventions are in common use, $\gamma = 0$ (the ZSHA convention [5]) and $\gamma = \pi/2$ (the H convention [3]). In either case inversion of the spatial coordinates, in which $(X, Y, Z) \rightarrow$

$(-X, -Y, -Z)$, is equivalent to reflection of the electronic coordinates in a plane passing through the internuclear axis, followed by a two-fold rotation about an axis perpendicular to this plane acting on the rotational wavefunctions [3]. In the ZSHA phase convention this is expressed as

$$i_{\text{sp}} = \sigma_v^{yz} C_2^x, \quad (3a)$$

while in the H convention

$$i_{\text{sp}} = \sigma_v^{xz} C_2^y. \quad (3b)$$

In consequence, the phases of $|n\Lambda\Sigma\rangle$ and $|JM\Omega\rangle$ under i_{sp} are different for the two conventions, but the product is identical, namely \ddagger

$$i_{\text{sp}} |n\Lambda\Sigma\rangle |JM\Omega\rangle = (-1)^{J-S} |n-\Lambda S-\Sigma\rangle |JM-\Omega\rangle. \quad (4)$$

The electronic function $|n\Lambda\Sigma\rangle$ can be written rigorously as $|n\Lambda\rangle |S\Sigma\rangle$ only for a one- or two-electron system, for which the electronic wavefunction can be factorised into space and spin functions. However, for more than two electrons the wavefunction can always be represented as an antisymmetric combination of such product functions. Hence, for understanding the transformation properties under symmetry operations, we need only consider one such product.

Implicit in the derivation of eqs. (1) and (4) is the convention that

$$\sigma_v^{xz} |n\Lambda\rangle = (-1)^\Lambda |n-\Lambda\rangle \quad (5a)$$

and

$$\sigma_v^{yz} |n\Lambda\rangle = |n-\Lambda\rangle. \quad (5b)$$

This is equivalent to writing

$$|n\Lambda\rangle = (-1)^\Lambda \Psi_{|\Lambda|} \exp(i\Lambda\phi_e) \quad (6a)$$

and

\ddagger In ref. [5] the overall phase factor under inversion of the space-fixed coordinate frame is given as $(-1)^{J+S}$ for $\Lambda \neq 0$ states. For even-electron systems (with integral S) this is completely equivalent to $(-1)^{J-S}$, while for odd-electron systems (half-integral S) this reverses the parity of each wavefunction. For an isolated system such a change has no physical consequences. As first pointed out by Larsson [10], ref. [5] mixed the active and passive points of view in deriving this phase factor. Eq. (A19) of ref. [5] should be replaced by its complex conjugate, thereby giving the overall phase of $(-1)^{J-S}$.

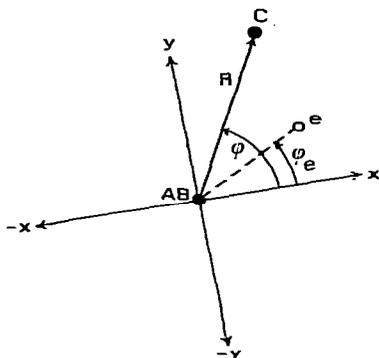


Fig. 1. The relationship between the electronic orbital and collisional coordinates as viewed along the molecule-fixed z -axis (the internuclear axis of the AB target). Here R is the position vector connecting C and AB, and its azimuthal angle ϕ is measured from the xz plane of the AB frame, as is the angle ϕ_e describing the azimuthal angle conjugate to the orbital angular momentum vector Λ of AB.

$$|n - \Lambda\rangle = \Psi_{|\Lambda|} \exp(-i\Lambda\phi_e), \quad (6b)$$

where $\Psi_{|\Lambda|}$ is the orientation-independent part of the electronic orbital wavefunction, and ϕ_e expresses the azimuthal angle dependence measured from the x -axis of the molecule-fixed frame.

Let a collision partner approach, as shown in fig. 1. Its azimuthal angle must be defined *with respect to the same x -axis*. For simplicity we take the collision partner as structureless, and concentrate on the ϕ dependence of the stationary state wavefunctions for the colliding partners, which is:

A' state:

$$\begin{aligned} \Psi_e' &\propto \Psi_{|\Lambda|} \cos \Lambda(\phi - \phi_e) \\ &= \frac{1}{2} [(-1)^\Lambda \exp(-i\Lambda\phi)|n\Lambda\rangle + \exp(i\Lambda\phi)|n - \Lambda\rangle]; \end{aligned} \quad (7a)$$

A'' state:

$$\begin{aligned} \Psi_e'' &\propto \Psi_{|\Lambda|} \sin \Lambda(\phi - \phi_e) \\ &= \frac{1}{2} i [(-1)^\Lambda \exp(-i\Lambda\phi)|n\Lambda\rangle - \exp(i\Lambda\phi)|n - \Lambda\rangle]. \end{aligned} \quad (7b)$$

The system described by the electronic wavefunction Ψ_e' interacts over a potential surface $V'(R) = \langle e'' | H_{\text{eff}} | e' \rangle$, and that described by Ψ_e'' over a surface

$V''(R) = \langle e'' | H_{\text{eff}} | e'' \rangle$, where R is the position vector connecting the centres of mass of the collision partners (and $V(R)$ is the interaction potential). In evaluating matrix elements of the interaction potential over the full scattering basis it is essential to carry through the electronic phase factor $(-1)^\Lambda$ of eqs. (6) and (7).

The theoretical treatment of Dixon and Field [17] made use of the "perturbed stationary state" method, in which a potential is constructed which acts only in the space of the nuclear coordinates, following earlier work by Bates [25], as generalised by Green and Zare [6] to molecular problems. In this treatment the matrix elements of the effective interaction Hamiltonian over the electronic basis of eq. (6) become

$$\langle n\Lambda | H_{\text{eff}} | n\Lambda \rangle = \langle n - \Lambda | H_{\text{eff}} | n - \Lambda \rangle = V_0(R) \quad (8a)$$

and

$$\begin{aligned} \langle n - \Lambda | H_{\text{eff}} | n\Lambda \rangle &= \langle n\Lambda | H_{\text{eff}} | n - \Lambda \rangle^* \\ &= V_{2\Lambda}(R) \exp(2i\Lambda\phi), \end{aligned} \quad (8b)$$

where R lies in the scattering plane (eq. (3) of ref. [17]). The effective potentials $V_0(R)$ and $V_{2\Lambda}(R)$ are related to the Born-Oppenheimer potentials of the stationary states of the collision system through

$$V_0(R) = \frac{1}{2} [(V'(R) + V''(R))] \quad (9a)$$

and

$$V_{2\Lambda}(R) = \frac{1}{2} (-1)^\Lambda [V'(R) - V''(R)]. \quad (9b)$$

Eqs. (9) differ from eq. (4) of ref. [17] by the inclusion of the phase factor $(-1)^\Lambda$ in (9b). No other equation in ref. [17] needs to be changed apart from this and the corresponding changes to eq. (6) for collision partners with spin.

This change has no consequence for even Λ (e.g. Δ states), but reverses the signs of the matrix elements of $V_{2\Lambda}(R)$, (and thus of its spherical harmonic component $V_{2,2}(R)$ [17]), for odd Λ (e.g. Π states, such as OH and CH).

In summary, the use of the full machinery of angular momentum coupling theory requires a curious choice of the phase factor of the electronic wavefunctions, as first pointed out by Condon and Shortley [26] for atoms. It is the incorporation of this phase factor into eq. (4) which carries through into the sense of the anisotropy of the interaction potential, as shown in eq. (9). This sign change is independent of

the choice of a case (a) basis, as in eq. (1), or a case (b) basis, as in ref. [17]. This problem arises only for partners with electronic orbital degeneracy: conclusions for molecules with K -doubling, such as H_2CO [2] and NH_2 [27], are not affected.

3. Consequences for mechanisms of celestial OH maser action

One of the most remarkable events in radio-astronomy was the observation in 1965 [28] of maser action involving transitions across the ground-state Λ -doublet of OH. Masers are of considerable interest since they are found in regions of stellar formation (e.g. W3(OH)) and in the atmospheres of late-type stars [29,30]. A variety of possible mechanisms has been proposed for the generation of Λ -doublet population inversion in OH [30]. These include optical pumping cycles, photochemical generation, and combinations of collisional and radiative processes.

The last of these mechanisms has been discussed by Dixon and Field [17,18] among other authors. Accurate interaction potentials were not available to Dixon and Field at that time, and they based their conclusions on crude valence-bond considerations ‡.

Subsequent ab initio calculations on OH + H_2 by Walch and Dunning [33] and by Kochanski and Flower [34] have upheld the sense deduced in ref. [17] for the anisotropy, namely that the lowest energy configuration is that in which the unpaired π -electron of OH is directed towards H_2 . However, the missing phase factor in eq. (4) of ref. [17] (see eq. (9)) has the consequence of reversing several of the conclusions in that paper. We restate here the revised predictions for OH(OD) + H_2 collisions based on the consistent treatment of the azimuthal dependence of the interaction potential:

(i) rotationally inelastic collisions can lead to the

* Dixon and Field also discussed collisional inversion in CH. In view of the results presented here, predictions regarding CH Λ -doublet populations must now be reversed, provided that the anisotropy of the interaction potential assumed by Dixon and Field proves to be correct. Results reported in a recent paper on CH emission [31] therefore stand in need of modification, as also do certain conclusions reached in a paper on OH masers [32].

inversion of certain pairs of Λ -doublet levels of OH and OD;

(ii) collisions involving energy transfer out of $F_1(1\frac{1}{2})$ result in cooling (anti-inversion) in $F_1(2\frac{1}{2})$ and $F_1(3\frac{1}{2})$;

(iii) collisions involving energy transfer out of $F_1(1\frac{1}{2})$ result in inversion of $F_2(\frac{1}{2})$, $F_2(1\frac{1}{2})$ and $F_2(2\frac{1}{2})$;

(iv) the presence of hyperfine structure will not qualitatively affect the conclusions as to whether a pair of Λ -doublets is cooled or inverted by rotational energy transfer.

Andresen, Häusler and Lülff [16] recently carried out a pulsed crossed beam study of rotationally cold OH + H_2 collisions, in which laser-induced fluorescence was used to monitor the resulting OH Λ -doublet populations for various J levels of the F_1 and F_2 manifolds. Starting with OH molecules predominantly in $F_1(1\frac{1}{2})$, they report cooling of the Λ -doublet populations transferred within the F_1 manifold, the extent of which increases with increasing J . By contrast the F_2 manifold shows a tendency to inversion which increases with increasing J . Thus the revised predictions of Dixon and Field outlined in (ii) and (iii) support the conclusions that a collisional mechanism by itself cannot account for OH maser action in $F_1(1\frac{1}{2})$, but might be an important process leading to maser action in $F_2(\frac{1}{2})$.

Acknowledgement

RND and DF are grateful to the UK Science and Engineering Research Council, and RNZ to the US National Science Foundation, for their support for this research over a number of years. RND and RNZ also appreciate the award of a NATO grant (141.82).

References

- [1] R.S. Mulliken and A. Christy, *Phys. Rev.* 38 (1931) 87.
- [2] C.H. Townes and A.C. Cheung, *Astrophys. J.* 157 (1969) L103.
- [3] J.T. Hougen, *Natl. Bur. Std. (US) Monograph* 115 (1970).
- [4] I. Røeggen, *Theoret. Chim. Acta* 21 (1971) 398.
- [5] R.N. Zare, A.L. Schmeltekopf, W.J. Harrop and D.L. Albritton, *J. Mol. Spectry.* 46 (1973) 37.
- [6] S. Green and R.N. Zare, *Chem. Phys.* 7 (1975) 62.

- [7] M. Bertojo, A.C. Cheung and C.H. Townes, *Astrophys. J.* 208 (1976) 914.
- [8] J.J. ter Meulen, W.L. Meerts, G.W.M. van Mierlo and A. Dymanus, *Phys. Rev. Letters* 36 (1976) 1031.
- [9] R.P. Mariella Jr. and A.C. Luntz, *J. Chem. Phys.* 57 (1977) 5788.
- [10] M. Larsson, *Physica Scripta* 23 (1981) 835.
- [11] E.J. Murphy, J.H. Brophy, G.C. Arnold, W.F. Dimpfl and J.L. Kinsey, *J. Chem. Phys.* 74 (1981) 324.
- [12] J.L. Kinsey, *J. Chem. Phys.* 81 (1984) 6410.
- [13] D.P. Dewangan and D.R. Flower, *J. Phys.* B18 (1985) L137.
- [14] M.H. Alexander and P.J. Dagdigian, *J. Chem. Phys.* 80 (1984) 4325.
- [15] Ch. Ottinger, R. Velasco and R.N. Zare, *J. Chem. Phys.* 52 (1970) 1636.
- [16] P. Andresen, D. Häusler and H.W. Lülf, *J. Chem. Phys.* 81 (1984) 571.
- [17] R.N. Dixon and D. Field, *Proc. Roy. Soc.* A368 (1979) 99.
- [18] R.N. Dixon and D. Field, *Mon. Not. Roy. Astron. Soc.* 189 (1979) 583.
- [19] H. Kaplan and M. Shapiro, *Astrophys. J.* 229 (1979) L91.
- [20] D.P. Dewangan and D.R. Flower, *J. Phys.* B14 (1981) 2179; *Mon. Not. Roy. Astron. Soc.* 199 (1982) 457; *J. Phys.* B16 (1983) 2157.
- [21] P. Andresen, G.S. Ondrey, B. Titze and E.W. Rothe, *J. Chem. Phys.* 80 (1984) 2548.
- [22] R. Vasudev, R.N. Zare and R.N. Dixon, *J. Chem. Phys.* 80 (1984) 4863.
- [23] J.M. Brown, J.T. Hougen, K.-P. Huber, J.W.C. Johns, I. Kopp, H. Lefebvre-Brion, A.J. Merer, D.A. Ramsay, J. Rostas and R.N. Zare, *J. Mol. Spectry.* 55 (1975) 500.
- [24] I. Kopp and J.T. Hougen, *Can. J. Phys.* 45 (1967) 2581.
- [25] D.R. Bates, *Atomic and molecular processes* (Academic Press, New York, 1962) p. 597.
- [26] E.U. Condon and G.H. Shortley, *The theory of atomic spectra* (Cambridge Univ. Press, Cambridge, 1963) p. 52.
- [27] R.N. Dixon and D. Field, *Proc. Roy. Soc.* A366 (1979) 225, 247.
- [28] H. Weaver, D.R.W. Williams, N.H. Dieter and W.T. Lum, *Nature* 208 (1965) 29.
- [29] A.H. Cook, *Celestial masers* (Cambridge Univ. Press, Cambridge, 1977).
- [30] M. Elitzur, *Rev. Mod. Phys.* 54 (1982) 12, and references therein.
- [31] D. Bouloy, N.Q. Rieu and D. Field, *Astron. Astrophys.* 130 (1984) 380.
- [32] D. Field, *Mon. Not. Roy. Astron. Soc.* 201 (1982) 527.
- [33] S.P. Walch and T.H. Dunning, *J. Chem. Phys.* 72 (1980) 1303.
- [34] E. Kochanski and D.R. Flower, *Chem. Phys.* 57 (1981) 217.