

Effect of anisotropy on the glory structure of molecule-molecule scattering cross sections

Jesús Pérez-Ríos ^a, Massimiliano Bartolomei,

José Campos-Martínez and Marta I. Hernández

Instituto de Física Fundamental, Consejo Superior de Investigaciones

Científicas (IFF-CSIC), Serrano 123, 28006 Madrid, Spain

(Dated: December 9, 2011)

Abstract

Total (elastic + rotationally inelastic) integral cross sections are computed for $O_2(^3\Sigma_g^-)$ - $O_2(^3\Sigma_g^-)$ using a recent ab initio potential energy surface. The sampled velocity range allows us a thorough comparison of the glory interference pattern observed in molecular beam experiments. The computed cross sections are about 10% smaller than the measured ones, however, a remarkable agreement in the velocity positions of the glory extrema is achieved. By comparing with models where the anisotropy of the interaction is reduced or removed, it is found that the glory pattern is very sensitive to the anisotropy, especially the positions of the glory extrema.

^a Electronic mail: jpr@iff.csic.es

I. INTRODUCTION

The velocity dependence of total integral cross sections in molecular beam experiments usually shows an oscillatory pattern in the thermal and epithermal regimes. These glory undulations arise from a quantum-mechanical interference of scattered waves for interaction potentials exhibiting wells, and indeed the number of oscillations are related to the number of bound states of the scattering potential[1]. Glory undulations have been observed in atom-atom[2–5] and in atom-molecule[6–9] collisions, and they have served to extract some features of the intermolecular interaction, in particular, the spherically averaged or isotropic term of the Potential Energy Surface (PES)[2–4, 9, 10]. Atom-molecule interactions do depend on the angles of orientation of the molecule relative to the atom, and the effects of the anisotropy on the cross sections, typically producing a damping of the glory oscillations, have been widely studied [7–9, 11–14]. However, and despite there have been many experimental studies of molecule-molecule collisions[15–18], the role of anisotropy for these more complex interactions has been seldom studied from a theoretical point of view.

Recently, a high level global *ab initio* PES including the singlet, triplet and quintet multiplicities of the $O_2(^3\Sigma_g^-)$ - $O_2(^3\Sigma_g^-)$ system has been reported by Bartolomei *et al*[19]. The interaction includes long-range coefficients obtained from first principles calculations of the electric properties of the monomers[20]. In order to study the performance of this PES, we have carried out some dynamical calculations at different energy regimes including ultracold[21], cold[22], and preliminary calculations in the thermal regime[19, 23]. For cold translational temperatures, $10 \leq T_t$ (K) ≤ 34 , the quality of the *ab initio* PES was tested against measurements of rotational populations of O_2 molecules traveling along a supersonic jet[22]. Close-coupling calculations of rotationally inelastic state-to-state rate coefficients were found in good agreement with the experimental data, suggesting that the anisotropy of the *ab initio* PES is realistic. On the other hand, second virial coefficients computed using the *ab initio* PES compare quite well with experimental values over a wide range of temperatures, and it was checked that including the full anisotropy of the interaction is crucial to achieve such an agreement[19, 24].

In a higher energy regime, Aquilanti *et al* reported total cross sections measurements for O_2 - O_2 using rotationally hot effusive beams[15]. These and analogous measurements using colder supersonic seeded beams, together with second virial coefficient data, allowed the

authors to obtain an experimentally derived PES, the Perugia PES from now on. In this way, cross section calculations just using the spherical average of the Perugia PES showed quite a good comparison with the effusive beam experiments[15]. However, analogous calculations using the recent *ab initio* PES showed some discrepancies with the experimental data[19]. The effect of the anisotropy in the behavior of the total integral cross sections has been only partially studied by means of close-coupling calculations for a lower energy range and only using the quintet PES[23].

In this work, we extend previous work[19, 23] by computing total (elastic + rotationally inelastic) integral cross sections in the relevant energy range and considering the fully anisotropic PES for the three spin multiplicities involved. The coupled-states approximation[25–27] is used. Our aim is to provide a sensible test of the *ab initio* PES in the thermal regime by comparison with the experiments of Ref.[15]. In this regard, we also study how and how much the anisotropy of the interaction affects the structure of the glory undulations in the case of molecule-molecule collisions.

The paper is organized as follows. In Section II, we give a short summary on the theory and computational details. Results are reported and discussed in section III, and conclusions are given in section IV.

II. THEORY AND COMPUTATIONAL DETAILS

The collision dynamics of O₂+O₂ is studied within the rigid rotor approximation and neglecting the fine structure. The theory for the scattering of two identical linear rigid rotors has been reviewed in Ref.[23] and applied to O₂+O₂ elsewhere[22, 23], so here we focus in some aspects specific to this study. Using diatom-diatom Jacobi vectors \mathbf{R} , \mathbf{r}_1 , and \mathbf{r}_2 in a space-fixed frame, the Hamiltonian is written as (in atomic units) [28, 29],

$$H = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hat{l}^2}{2\mu R^2} + B_e \left(\hat{j}_1^2 + \hat{j}_2^2 \right) + V_M(\mathbf{R}, \hat{r}_1, \hat{r}_2) \quad (1)$$

where $B_e = 1.438 \text{ cm}^{-1}$ is the rotational constant of the ¹⁶O₂ molecules, $\mu = 15.9949 \text{ amu}$ is the reduced mass of the collision system and \hat{l} , \hat{j}_1 and \hat{j}_2 are angular momentum operators associated with \hat{R} , \hat{r}_1 and \hat{r}_2 , respectively. Moreover, V_M is the intermolecular PES for a given electronic spin of the complex ($M = S, T, Q$ for the singlet, triplet and quintet spin multiplicities, respectively). The time-independent close-coupling equations are separately

solved for each spin multiplicity (since the Hamiltonian commutes with the total electronic spin) and also, for each symmetry block of the G_{16} group, by using symmetry adapted bases associated to the spatial inversion, permutation operator within the monomers and simultaneous permutation of nuclei between the monomers[30]. Statistical weights appropriate to $^{16}\text{O}_2+^{16}\text{O}_2$ are taken as explained in detail in Refs.[22, 23]. Besides, for the present simulation of the number of particles lost from a molecular beam due to scattering by a target, the computed integral cross section must be corrected when the final states of the colliding partners are identical, in order to avoid a double counting[23]. In this way, the total (elastic + inelastic) integral cross section for a selected pair of initial rotational states (j_1, j_2) is

$$Q_{j_1, j_2}^M = \sum_{j'_1, j'_2} \frac{Q_{j'_1 j'_2, j_1 j_2}^M}{1 + \delta_{j'_1, j'_2}}, \quad (2)$$

where $Q_{j'_1 j'_2, j_1 j_2}^M$ is the state-to-state integral cross section for indistinguishable monomers as obtained by Takayanagi[31]. These cross sections are finally averaged using the multiplicity of each spin state as a statistical weight,

$$Q_{j_1, j_2} = \frac{5 Q_{j_1, j_2}^Q + 3 Q_{j_1, j_2}^T + Q_{j_1, j_2}^S}{9}. \quad (3)$$

Calculations have been carried out within the coupled-states (CS) approximation[25, 27] as implemented in the MOLSCAT code[32]. We used the global *ab initio* PES of Bartolomei *et al*[19] unless otherwise stated. The cross sections of Eq.3 were computed for kinetic energies ranging from 27 to 4873 cm^{-1} . The close-coupling equations were solved using the Alexander and Monolopoulos's hybrid log-derivative/Airy propagator [33]. The propagation was carried out from $R = 2.51 \text{ \AA}$ up to $R = 46.8 \text{ \AA}$, the switch between the log-derivative and the Airy propagator done at $R = 11.7 \text{ \AA}$. Calculations were performed for increasing numbers of the total rotational angular momentum J until convergence (the highest J reached was 606). For a given initial state, (j_1, j_2) , a total of twelve rotational states were included in the expansion of the total wave function, six of them having a internal energy lower than that of the initial state. By performing additional CS calculations with four additional rotational states, we have checked that the total cross sections are converged within about 2%.

It remains to check the validity of the CS approximation. It is expected that the CS approximation will work well when the kinetic energy becomes large as compared with the potential well depth[27, 34]. We have compared the CS calculations with fully coupled

calculations for kinetic energies ranging from 27 to 360 cm^{-1} (note that the $\text{O}_2\text{-O}_2$ well depth is of the order of 100 cm^{-1}). The error obtained was smaller than 5%. For the higher energy range, where the fully coupled calculations would become extremely expensive, the error of the CS approximation should be smaller.

III. RESULTS AND DISCUSSION

Present calculations are compared with the experimental results of Aquilanti *et al*[15]. In that experiment, the oxygen projectile is in a hot effusive beam at a high rotational temperature (500 K), and it collides with an oxygen target in a reaction chamber at about 90 K. The most populated rotational states in these conditions are $j_1=9\text{-}13$ and $j_2=5$ for beam and target, respectively. Thus, we have chosen ($j_1=11, j_2=5$) as the initial state for the cross sections of Eq.3. Some additional calculations were performed using other populated states (e.g. $j_1=9, j_2=7$) and the results were found to be insensitive to these modifications in the simulation. The computed cross sections are obtained as functions of the kinetic energy or, equivalently, of the velocity in the center-of-mass frame. In order to compare with the experiments, they are transformed to functions depending of the velocity in the laboratory frame according to the procedure described in Ref.[35].

Results are reported in Fig. 1 (upper panel), where computed and measured total cross sections are plotted as functions of the velocity v in the laboratory frame. It can be seen that the computed cross sections are smaller than the measured ones for the complete velocity range, the relative error varying from less than 15 % for the lowest velocities to about 5 % for the highest ones. Although this could be termed as a fair agreement, it should be noted that a closer agreement between *ab initio* calculations and experiment has been achieved for other systems such as $\text{N}_2\text{-N}_2$, $\text{N}_2\text{-H}_2$ and $\text{C}_2\text{H}_2\text{-H}_2$ [16–18]. Possible reasons for this relative discrepancy in the absolute cross sections are discussed below. On the other hand, it is readily noticed that calculations and experiment agree quite well regarding the slopes of the curves as functions of the velocity. In the lower panel of Fig.1 and in order to make a clearer comparison of the glory pattern, we show the derivative of the cross sections with respect to the velocity. In this way, the performance of the PES in the well region is more conveniently tested. The agreement, it can be seen, can be termed as excellent. We have found that the

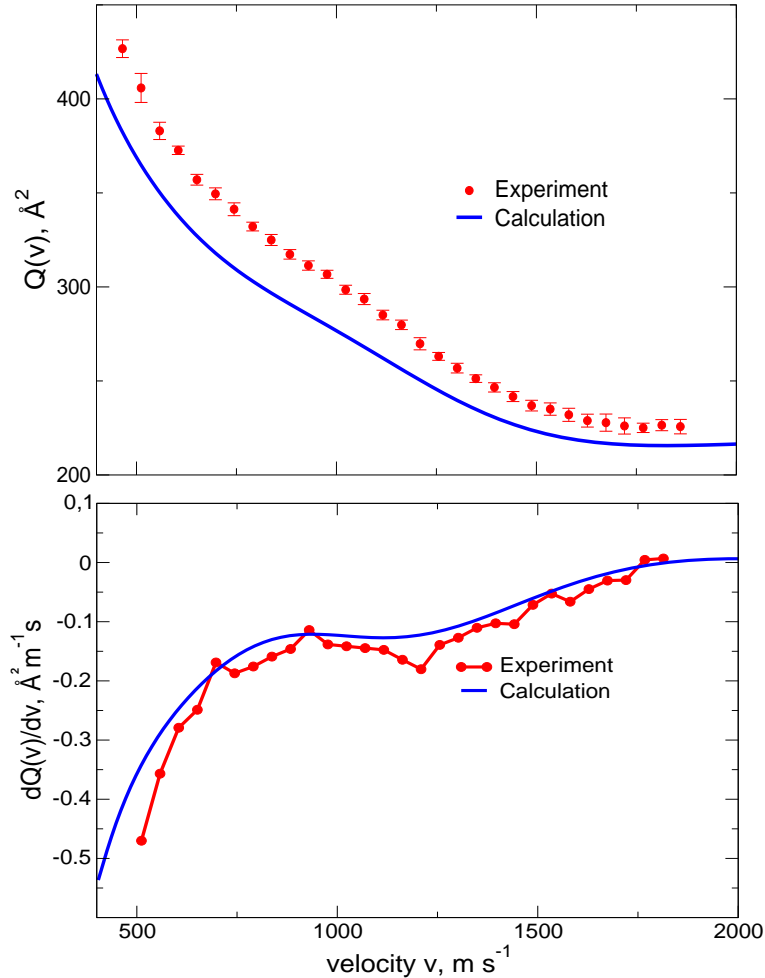


FIG. 1. (Color online) Upper panel: Total (elastic + inelastic) integral cross sections $Q(v)$ (in \AA^2) versus the velocity v in the laboratory frame (in m/s). The experimental data [15] are given by circles, while present calculations using the *ab initio* PES of Ref.[19] are shown using a solid line. Lower panel: Same as upper panel for the derivative of the total integral cross section with respect the velocity $dQ(v)/dv$ (in $\text{\AA}^2 m^{-1} s$) as a function of v .

detailed interference pattern is very sensitive to the anisotropy of the interaction. Indeed, agreement with the observed positions of the undulations is only achieved when the full anisotropy of the PES is included, as shown in the following analysis.

In Fig. 2 we present (solid lines) the individual cross sections for the singlet, triplet and quintet multiplicities, i.e., the ones entering in the average of Eq. 3. The cross sections are now shown multiplied by $v^{2/5}$ since it is known[36, 37] that the semiclassical $Q(v) \times v^{2/5}$ is proportional to $C_6^{2/5}$ for a C_6/R^6 interaction. In this way, the glory structure is emphasized

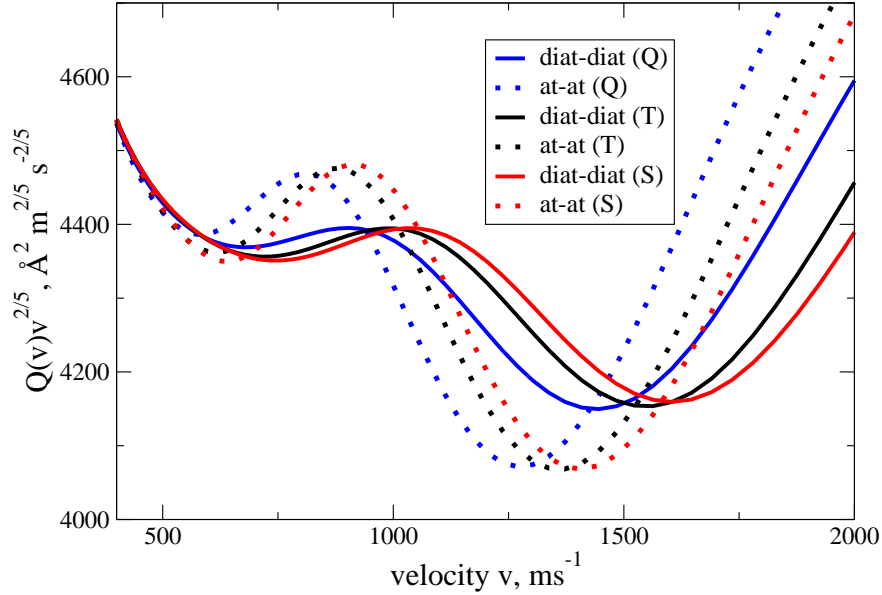


FIG. 2. (Color online) Total integral cross sections $Q(v)$ multiplied by $v^{2/5}$ (in $\text{\AA}^2 (m/s)^{2/5}$) as functions of the laboratory velocity, v (in m/s), for the different multiplicities of the *ab initio* PES[19] (Q, T, and S stand for quintet, triplet and singlet, respectively). Solid curves (“diat-diat”) are present calculations where the full anisotropy of the PES is included, whereas dotted curves (“atom-atom”) refer to approximate calculations where only the spherically averaged interaction is retained.

and the average value of $Q(v) \times v^{2/5}$ can be much easily related to the long range features of the interaction[15]. The calculations reported in Fig. 2 are compared with an “atom-atom” model (dotted lines), i.e., the cross sections for structureless particles interacting with the spherically averaged potential of each of the multiplicities. This approximation has been done by including only the the $(j_1, j_2) = (0, 0)$ rotational level and just the isotropic component of the interaction in the calculations.

The analysis presented in Fig.2 allows us to discuss the effects of both the *spatial* and the *spin* anisotropy on the glory structure of the cross sections, so several comments follow. First, note that the average value (disregarding glory oscillations) of the *total* cross section is very close to the average value of the (elastic) cross section in absence of anisotropy, i.e., it essentially depends of the features of the *isotropic* term of the interaction. This is the rule known as “the conservation of total cross section”, proposed and checked time ago[38, 39], and recently confirmed for the present system by us[23]. We have additionally checked that

such an average value agrees with an *effective* C_6 coefficient defined by the behavior of the isotropic potential in the range $R = 6\text{-}8 \text{ \AA}$ (note that, in this region, singlet, triplet and quintet interactions are almost identical). We have found that this “effective” C_6 value is due to contributions from C_6 , C_8 and higher order long-range coefficients[23]. Given the sensitivity of the absolute cross sections to slight modifications of the interaction energies, the fact that the computed cross sections are somewhat smaller than the measured ones (Fig.1, upper panel) could indicate some inaccuracies of the PES in that range of intermolecular distances.

A second aspect from Fig.2 is the modification of the glory structure due to the anisotropy of the interaction. For a given spin multiplicity, the effect of the anisotropy is a quenching of the oscillations as well as a shift of the glory extrema, as compared with the isotropic, atom-atom model. The effect is found more significant as compared with previous atom-diatom studies[11–14], particularly in the modification of the positions of the glory extrema (velocities giving maxima or minima in the glory pattern). For instance, a similar analysis for $\text{O}_2\text{-Kr}$ concluded that the anisotropy reduces the glory amplitude but does not modify such positions[9]. Finally and regarding the effect of the spin multiplicities, it is found that the positions of the glory extrema vary with the different multiplicities (owing to differences in the well regions, the singlet and quintet potentials having the largest and smallest well depths, respectively). This affects indeed the final glory structure after averaging (Eq. 3). However, by comparing the effect of the anisotropy with that of averaging the different spin multiplicities, it can be concluded that the anisotropy plays a more determinant role in the final shape of the cross sections.

As has been shown, the addition of the anisotropy of the interaction does change the glory structure of the total cross sections and thus the atom-atom model is inappropriate for a realistic simulation of the experiments. This is a somewhat surprising conclusion in view of previous studies of effusive beams of diatomic molecules scattered by target atoms[9]. Diatoms emerge from a hot effusive beam with a high rotational temperature and therefore the rotation period becomes short as compared with the collision time. In these conditions, the effects of the anisotropy should be small and the interaction could be approximated by its spherical average. In addition, inelastic probabilities are expected to be small since the energy gap for a rotational transition becomes increasingly large as the initial rotational state increases. The situation is different for diatom-diatom scattering

since in this case the distribution of rotational levels becomes more uniform. For O_2-O_2 , the average minimum energy gap is about 20 cm^{-1} for the relevant rotational levels, so that inelastic transitions may not seem such a rare event. Moreover, analyzing the experimental conditions in more detail[15], we find that the average rotational periods of beam and target are $\tau_r^{beam} \sim 1 \times 10^{-12} \text{ s}$ and $\tau_r^{target} \sim 2 \times 10^{-12} \text{ s}$, respectively. The collision time ranges from $\sim 2 \times 10^{-12} \text{ s}$ at the lowest experimental velocity to $\sim 5 \times 10^{-13} \text{ s}$ at the highest one. By comparing collision and rotational periods, we note that the O_2 in the beam may behave as a pseudo-atom for low velocities of the beam. However, this approximation seems much more severe for the target molecule, since its rotational period is larger and hence its relative orientation must play a role in the collision dynamics, even at low velocities of the beam.

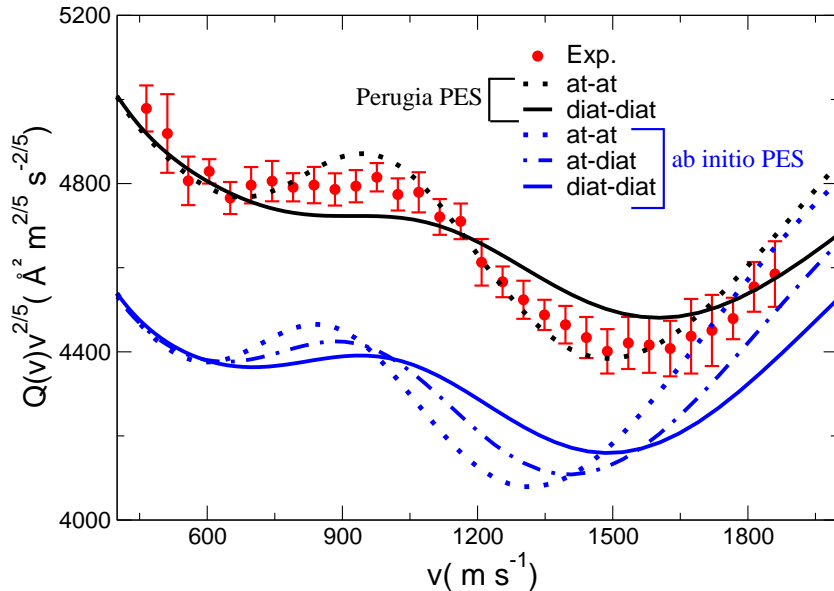


FIG. 3. (Color online) Total integral cross sections $Q(v)$ multiplied by $v^{2/5}$ (in $\text{\AA}^2 (m/s)^{2/5}$) as functions of the velocity (*ab initio* PES). The most accurate diatom-diatom calculation (full anisotropy, in solid lines) is compared with the more approximate atom-atom (isotropic) and atom-diatom (partially anisotropic) models (in dotted and dashed-dotted lines, respectively). Points with error bars represent the data of Aquilanti *et al*[15]. Analogous calculations using the experimentally derived Perugia PES[15] are also reported.

To test these ideas, we have considered an atom-diatom collisional model, where the atom represents the rotationally excited O_2 in the beam. To this end, we have included a set of

($j_1 = 0, j_2 = 1 - 11$) rotational levels in the calculations, and have computed the total integral cross section for the initial state ($j_1 = 0, j_2 = 5$) using the CS approximation. In this way, the terms in the PES effectively involved in the simulation are equivalent to those of an interaction potential between an atom and a rigid diatom. The total, spin averaged, cross sections are compared with those of the isotropic (atom-atom) and the fully anisotropic (diatom-diatom) models in Fig.3. Experimental data are also given in Fig. 3 as a guide to the eye. As expected, the results of the atom-diatom model lie in between those of the atom-atom and diatom-diatom calculations. While at low velocities of the beam all the results are nearly the same, in the intermediate range (800-1200 m/s) the atom-atom model becomes poor but the atom-diatom model still works well, indicating that in this range the rapid rotation of the molecule in the effusive beam is averaged. This approximation becomes worse for larger velocities ($v > 1200$) where the cross sections become more sensitive to the complete anisotropy of the interaction. It is worth to note that the values of the velocity positions of glory extrema vary very much with the different models studied, and that just the most accurate calculation gives the best agreement with the experimental positions. Finally, we have carried out calculations analogous to those explained here but using the experimentally derived Perugia PES, and results for the atom-atom model and the fully anisotropic calculation are also displayed in Fig. 3. It can be seen that the atom-atom model agrees quite well with the experiment: this is because some parameters of the isotropic Perugia PES were indeed fitted to the observed total cross sections. On the other hand, the effect of including the full anisotropy of the Perugia PES is very similar to that already reported for the *ab initio* PES: the glory amplitudes become quenched and positions of the extrema shift toward higher velocities as compared with the atom-atom, isotropic model.

IV. CONCLUSIONS

We have carried out calculations of total integral cross sections for the scattering of two rigid oxygen molecules aimed at testing a high level *ab initio* potential energy surface (PES) against effusive beam experiments in a broad range of beam velocities. The calculations are in excellent agreement with the measurements regarding the values of the beam velocities at which the cross sections exhibit maximum or minimum values in the glory structure. We

have shown that this agreement is only achieved when the full anisotropy of the interaction is included in the simulations. In this way and in contrast to accumulated experience in atom-molecule scattering, it is reported that anisotropy in molecule-molecule scattering not only produces a quenching in the glory amplitudes (with respect to a purely isotropic interaction) but also a significant shift in the positions of the glory extrema. This conclusion should be beared in mind when a potential inversion from measurements is attempted in the case of molecule-molecule scattering.

As for a more global assessment of the O₂-O₂ *ab initio* PES, it can be concluded that it is realistic as it reproduces very well the measured second virial coefficients, state-to-state rate coefficients at low temperature, and the glory structure of the cross sections discussed here. This conclusion mainly refers to the short-range anisotropy of the interaction as this property is determinant for the observables listed above. However the calculations underestimate (by about 10%) the experimental values of the total cross sections. As mentioned in the previous section, it is the region around 6-8 Å the responsible for the discrepancies between experimental and theoretical cross-sections. In this region the dominant contribution corresponds to the supermolecular calculation and, therefore, we would expect that a more accurate ab-initio calculation (small changes of about tenths of cm⁻¹) will bring the theoretical results much closer to the experimental one. In this regard it is worth noticing that among the three lowest surfaces corresponding to the singlet, triplet, and quintet multiplicities, only the latter has been computed at the highest level of theory, whereas the others have been obtained by differences using a lower level of theory [19, 40]. These complications would explain why in similar cases it was possible a much closer agreement between experiment and theory. Another possible factor might be the role played by the intramolecular spin-spin term (fine structure, neglected here) and its interplay with the different spin multiplicities of the intermolecular potential. Despite these possible improvements, it would be worthwhile to test the present PES against more refined or new types of measurements.

V. ACKNOWLEDGMENTS

We acknowledge funding by Ministerio de Ciencia e Innovación (Spain, FIS2010-22064-C02-02). J.P.-R. is a JAE CSIC predoctoral fellow.

- [1] R. B. Bernstein, *J. Chem. Phys.* **37**, 1880 (1962).
- [2] R. B. Bernstein and R. A. LaBudde, *J. Chem. Phys.* **58**, 1109 (1973).
- [3] E. F. Greene and E. A. Mason, *J. Chem. Phys.* **57**, 2065 (1972).
- [4] R. B. Bernstein and R. J. P. O'Brien, *J. Chem. Phys.* **46**, 1208 (1967).
- [5] T. D. Roberts, A. D. Cronin, D. A. Kokorowski and D. E. Pritchard, *Phys. Rev. Lett.* **89**, 200406 (2002).
- [6] R. B. Bernstein, *J. Chem. Phys.* **34**, 361 (1961).
- [7] R. K. B. Helbing and E. W. Rothe, *J. Chem. Phys.* **48**, 3945 (1968).
- [8] E. A. Gislason and G. H. Kwei, *J. Chem. Phys.* **46**, 2838 (1967).
- [9] V. Aquilanti, D. Ascenzi, D. Cappelletti, M. de Castro Víttores, F. Pirani, *J. Chem. Phys.* **109**, 3898 (1998).
- [10] D. Cappelletti, V. Aquilanti, E. Cornichi, M. Moix Teixidor and F. Pirani, *J. Chem. Phys.* **123**, 024302 (2005).
- [11] J. R. Cross Jr., *J. Chem. Phys.* **49**, 1968 (1968).
- [12] R. E. Olson and R. B. Bernstein, *J. Chem. Phys.* **49**, 162 (1968).
- [13] W. H. Miller, *J. Chem. Phys.* **50**, 3124 (1969).
- [14] R. Goldflam, S. Green, D. J. Kouri and L. Monchick, *J. Chem. Phys.* **69**, 598 (1978).
- [15] V. Aquilanti, D. Ascenzi, M. Bartolomei, D. Cappelletti, S. Cavalli, M. de Castro Víttores, and F. Pirani, *J. Am. Chem. Soc.* **121**, 10794 (1999).
- [16] L. Gomez, B. Bussery-Honvault, T. Cauchy, M. Bartolomei, D. Cappelletti and F. Pirani, *Chem. Phys. Lett.* **445**, 99 (2007).
- [17] D. Cappelletti, F. Pirani, B. Bussery-Honvault, L. Gomez and M. Bartolomei, *Phys. Chem. Chem. Phys.* **4281**, 10 (2008).
- [18] F. Thibault, D. Cappelletti, F. Pirani and M. Bartolomei, *J. Phys. Chem. A* **113**, 14867 (2009).

- [19] M. Bartolomei, E. Carmona-Novillo, M. I. Hernández, J. Campos-Martínez and R. Hernández-Lamonedá, *J. Chem. Phys.* **133**, 124311 (2010).
- [20] M. Bartolomei, E. Carmona-Novillo, M. I. Hernández, J. Campos-Martínez and R. Hernández-Lamonedá, *J. Comput. Chem.* **32**, 279 (2011).
- [21] J. Pérez-Ríos, J. Campos-Martínez and M. I. Hernández, *J. Chem. Phys.* **134**, 124310 (2011).
- [22] J. Pérez-Ríos, G. Tejada, J. M. Fernández, M. I. Hernández and S. Montero, *J. Chem. Phys.* **134**, 174307 (2011).
- [23] J. Pérez-Ríos, M. Bartolomei, J. Campos-Martínez, M. I. Hernández and R. Hernández-Lamonedá, *J. Phys. Chem. A* **113**, 14952 (2009).
- [24] W. Wagner, J. Ewers and R. Schmidt, *Cryogenics* **84**, 37 (1984).
- [25] P. McGuire and D.J. Kouri, *J. Chem. Phys.* **60**, 2488 (1974).
- [26] R. T Pack, *J. Chem. Phys.* **60**, 633 (1974).
- [27] T. G. Heil, S. Green and D. J. Kouri, *J. Chem. Phys.* **68**, 2562 (1978).
- [28] S. Green, *J. Chem. Phys.* **62**, 2271 (1975).
- [29] W. H. Miller, *Dynamics of Molecular Collisions* (Plenum Press, New York, 1976).
- [30] A. van der Avoird and A. Brocks, *J. Chem. Phys.* **87**, 5346 (1987).
- [31] K. Takayanagi, *Progr. Theoret. Phys. (Kyoto) Suppl.* **25**, 1 (1963).
- [32] J. M. Hutson and S. Green, *MOLSCAT version 14* (Collaborative Computational Project No. 6 of the UK Science and Engineering Research Council, 1994).
- [33] D. E. Manolopoulos and M. H. Alexander, *J. Chem. Phys.* **86**, 2044 (1987).
- [34] D. J. Kouri, T. G. Heil and Y. Shimoni, *J. Chem. Phys.* **65**, 1462 (1976).
- [35] D. Cappelletti, M. Bartolomei, V. Aquilanti and F. Pirani, *J. Phys. Chem. A* **106**, 10764 (2002).
- [36] L. I. Schiff, *Phys. Rev.* **103**, 443 (1956).
- [37] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press Ltd., London, 1959).
- [38] R. D. Levine, *J. Chem. Phys.* **57**, 1015 (1972).
- [39] J. Eccles and D. Secrest, *J. Chem. Phys.* **67**, 5115 (1977).
- [40] M. Bartolomei, M. I. Hernández, J. Campos-Martínez, E. Carmona-Novillo and R. Hernández-Lamonedá, *Phys. Chem. Chem. Phys.* **10**, 5374 (2008).