

Theoretical determination of the intermolecular potentials of the C_2-H_2 system. Application to the collisional deexcitation of C_2 in collisions with H_2

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Abstract. Rotational deexcitation cross-sections are calculated for C_2 ground state by collisions with H_2 in an IOS treatment after the relevant potential surfaces have been determined. The corresponding rates are then determined for temperatures relevant to interstellar clouds.

Key words: collisions – interstellar matter – configuration interaction

1. Introduction

The C_2 molecule has been discovered in interstellar clouds (Souza & Lutz 1977) while its presence had been predicted from a chemical model (Black & Dalgarno 1977). Then, a lot of observations has been devoted to this molecule with high spectral resolution which provided column densities of the rotational levels of this molecule in its ground vibrational state up to $J = 14$ (e.g. Snow 1978; Chaffee & Lutz 1978; Hobbs 1979; Chaffee et al. 1980; Cosmovici & Strafella 1981; Hobbs & Campbell 1982; Danks & Lambert 1983; Van Dishoeck & De Zeew 1984; Van Dishoeck & Black 1986). The various level populations cannot be characterized by a single excitation temperature and a detailed description of various processes has to be taken into account for a reliable interpretation.

Radiative processes have already been the subject of theoretical calculations (Van Dishoeck & Black 1982; Pouilly et al. 1983; Le Boulrot & Roueff 1986; Le Boulrot et al. 1987). Collisional processes have only been estimated (Van Dishoeck & Black 1982). We consider here the problem of the ab-initio determination of the rotational deexcitation of C_2 colliding with H_2 , which is the most important component in interstellar clouds.

We present in the second section the calculations of the relevant potential surfaces. In Sect. 3, we summarize the infinite order sudden (IOS) approximation of the rotational deexcitation of C_2 and discuss the results obtained for the cross-sections and rate coefficients.

2. Intermolecular potential curves

The computational technique has been described previously in Lavendy et al. (1987, 1990). The basis set of gaussian functions must satisfy simultaneously two criteria: it must be large enough to give a reliable description of each molecule and also allow for the distortion of the electronic cloud of a molecule in the field of another molecule. To satisfy the first of these requirements we use for the H atoms the (9s, 4p) gaussian basis set of Siegbahn & Liu (1978) that we contract to (4s, 3p) and we use the (11s, 7p) basis set of Huzinaga & Sakai (1969) contracted to (6s, 4p) for the C atoms. We add one *d* (exponent = 0.79) orbital on each carbon atom to allow for a correct correlation of the π molecular shell and to improve the polarisability of the molecule. We assume that the criterion of a good description of the static dipole polarisabilities can give useful information about the latter aspect of the problem, namely dispersion interaction.

The valence shell of molecular orbitals is composed of the set of the self-consistent field (SCF) occupied orbitals of a ground state calculation of each partner C_2 and H_2 completed by optimised virtual orbitals, which are determined by means of the polarised atomic orbital (PAO) technique. A second shell of virtual orbitals is added, whose specific role is to account for the dispersion energy when the two partners approach each other. This shell is obtained from the distortion of the SCF occupied orbitals when a charge is placed along or perpendicularly to the internuclear axis. When the set of molecular orbitals is defined, the configuration interaction (CI) furnishes the electronic correlation by taking into account the effect of all spin and symmetry adapted configurations obtained by excitations from the closed shell ground state configuration. For H_2 , we found $\alpha_{||} = 6.16$ AU and $\alpha_{\perp} = 4.70$ AU and for C_2 $\alpha_{||} = 23.2$ AU and $\alpha_{\perp} = 11.1$ AU at the CI level. Concerning H_2 , our values are in good agreement with other theoretical results (see Lavendy et al. 1987 and references therein) while for C_2 no previous value is available.

To calculate the interaction energy of the supermolecule C_2-H_2 , the individual sets of molecular orbitals of each partner are orthogonalised for each geometry. The CI space consists of the direct product of CI spaces used in C_2 and H_2 polarisability calculations. It contains all excitations up to hexaexcitations in the valence shell. Hence we obtain the main part of the correlation

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Table 1. Interaction energies and (BSSE) for five selected geometries of the C_2-H_2 system^a

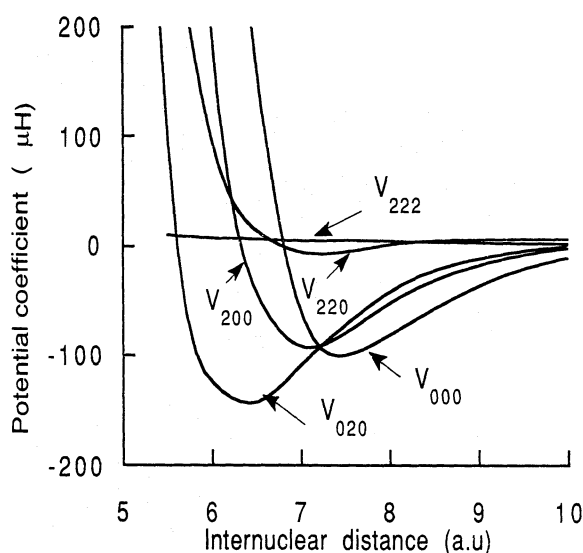
| R (AU) | Perpendicular | | Parallel | | T | Linear | | Crossed | |
|----------|---------------|-----|----------|----|-------|-----------|----------|---------|--|
| 5.0 | 4961 | 108 | 5554 | 56 | 11223 | 246 22567 | 398 5473 | 51 | |
| 5.5 | 1389 | 76 | 2333 | 37 | 4110 | 162 6985 | 253 2317 | 35 | |
| 6.0 | 189 | 62 | 967 | 23 | 1254 | 100 1542 | 170 954 | 23 | |
| 6.5 | -141 | 50 | 400 | 14 | 193 | 56 -182 | 93 379 | 14 | |
| 7.0 | -188 | 35 | 169 | 8 | -132 | 29 -538 | 51 143 | 8 | |
| 7.5 | -159 | 22 | 76 | 5 | -184 | 15 -465 | 26 49 | 5 | |
| 8.0 | -119 | 13 | 36 | 2 | -154 | 8 -285 | 14 13 | 2 | |
| 8.5 | -83 | 8 | 18 | 0 | -112 | 3 -162 | 6 0 | 0 | |
| 9.0 | -57 | 4 | 11 | 0 | -77 | 0 -73 | 2 -4 | 0 | |
| 10.0 | -31 | 0 | 7 | 0 | -38 | 0 | 0 -4 | 0 | |
| 12.0 | -13 | 0 | 3 | 0 | -12 | 0 | 0 -2 | 0 | |

^a All quantities are expressed in 10^{-6} AU. The energy reference is taken at $R = 30$ AU for all geometries. In each column, the first entry is the interaction energy and the second column gives the BSSE.

energy, including the angular correlation, and part of the dispersion energy. Monoexcitations from most important valence configurations into the second shell of virtual orbitals account for polarisation effects while simultaneous monoexcitations on each fragment give the remaining part of the dispersion energy. A lot of specific excitations are finally added to compensate for the dissymmetry of the orthogonalisation process; we have verified the efficiency of this procedure in computing the supersystem energy with two differently orthogonalised sets of molecular orbitals: the energy difference never exceeds 3%. About 3500 configurations are considered in the CI matrix. The interaction energy is defined as the difference between the energy of the supermolecule and the sum of the energies of the two fragments at each geometry. This interaction energy is generally overestimated due to the basis set superposition error (BSSE). We give in Table 1 corrected interaction energies using the Boys-Bernardi (1970) counterpoise method for the five different geometries studied as well as the corresponding BSSE. We notice that the collinear situation gives rise to the deepest potential well, and then we find the T and the perpendicular geometries. The potentials of the two other geometries are repulsive. We observe that the BSSE remains small, especially near Van der Waals minimum and we think that this is related to the use of molecular localized orbitals combined with selected CI in which only monoexcitations on each fragment are allowed in the dispersion CI contribution. To be tractable with collision calculations, ab-initio potentials are expanded in terms of body fixed coordinates as done by Danby & Flower (1983)

$$V(r_1, r_2, R) = \sum_{q_1 q_2 \mu \geq 0} V_{q_1 q_2 \mu}(R) Y_{q_1 q_2 \mu}(r_1, r_2).$$

Figure 1 displays the R -dependence of the first five terms of this development. We see that the isotropic term exhibits a minimum of about $-100.1 \cdot 10^{-6}$ AU at $R = 7.5$ bohrs. The term V_{200} which characterizes the anisotropic part of the potential responsible for the rotational excitation of C_2 has about the same amplitude, but its minimum is located at shorter R . The term V_{020} is only responsible for the rotational excitation of H_2 and is more important in absolute value than the term V_{200} at short range. As it is not coupled to the V_{200} term, it cannot affect directly the rotational excitation of C_2 . The two last terms, V_{220} and V_{222} can

**Fig. 1.** R -dependence of the first five terms of the potential

be neglected because they are too small to affect sensibly the calculated cross-sections.

3. Cross sections calculations

We performed scattering calculations with the IOS approximation for the rotational excitation of C_2 by para-hydrogen ($J=0$). In this case, the relevant angle dependence of the interaction reduces to two terms:

$$V(r_1, r_2, R) = V_{000}(R) + V_{200}(R) P_2(\cos \theta),$$

where θ is the angle between the C_2 molecule axis and the line connecting the centers of mass of the two molecules. Since we are essentially interested in low collision energies, the long range behaviour of the intermolecular potential has to be known.

Table 2. C₂ deexcitation rate coefficients in units of cm³ s⁻¹ for collisions with H₂ (*J*=0)^a

| <i>T</i> (K) | 100 | 300 | 500 | 1000 |
|------------------|-----------|-----------|-----------|-----------|
| <i>k</i> (2→0) | 1.3 (−11) | 1.4 (−11) | 1.6 (−11) | 2.9 (−11) |
| <i>k</i> (4→2) | 2.5 (−11) | 2.2 (−11) | 2.4 (−11) | 4.5 (−11) |
| <i>k</i> (6→4) | 4.1 (−11) | 2.8 (−11) | 2.9 (−11) | 5.2 (−11) |
| <i>k</i> (8→6) | 2.6 (−11) | 2.5 (−11) | 3.0 (−11) | 5.6 (−11) |
| <i>k</i> (10→8) | | 3.3 (−11) | 3.6 (−11) | 6.3 (−11) |
| <i>k</i> (12→10) | | 3.4 (−11) | 4.0 (−11) | 7.1 (−11) |
| <i>k</i> (14→12) | | 3.9 (−11) | 4.7 (−11) | 8.0 (−11) |
| <i>k</i> (16→14) | | 4.9 (−11) | 5.7 (−11) | 9.2 (−11) |
| <i>k</i> (18→16) | | 5.6 (−11) | 6.9 (−11) | 1.1 (−10) |

^a Numbers in parentheses are powers of 10

The isotropic term $V_{000}(R)$ reduces to the dispersion term

$$-\frac{3}{2} \frac{U_1 U_2}{U_1 + U_2} \frac{\alpha_1 \alpha_2}{R^6}$$

(see Buckingham 1968) where U_1 and U_2 are the ionization energies of C and H and α_1 and α_2 are the mean polarizabilities of the two molecules. The anisotropic term V_{200} involves the difference between the parallel and perpendicular polarizabilities of the C₂ molecule which have been determined in the previous section.

The numerical values of the V_{000} and V_{200} terms of the potential surface are extended with the analytic long range expressions. Goldflam et al. (1977) have shown that the IOS approximation is very effective in reducing computational labor involved in the calculations of S matrix elements relevant for collisional excitation of a diatomic molecule. One is indeed left with a system of uncoupled second order differential equations with L as a parameter from which one derives S_L matrix from usual asymptotic conditions:

$$\left\{ \frac{d^2}{dR^2} + k^2 - \frac{L(L+1)}{R^2} - 2\mu (V_{000}(R) - V_{200}(R) P_2(\cos \theta)) \right\} f(R, \theta) = 0. \quad (1)$$

The body fixed S matrix is obtained from averaging over the different orientations:

$$S_L(j, j') = 2\pi \int_0^\pi Y_{j, m_j}(\theta, 0) S_L(\theta) Y_{j, m_j}(\theta, 0) \sin \theta d\theta. \quad (2)$$

The space-fixed S matrix is subsequently calculated:

$$S(jl, j'l') = i^{l+l'-L} (2l+1)^{1/2} (2l'+1)^{1/2} \sum_{m_j} \begin{pmatrix} j & l & J \\ m_j & 0 & -m_j \end{pmatrix} \begin{pmatrix} j' & l' & J \\ m_j & 0 & -m_j \end{pmatrix} S_L(j, j') \quad (3)$$

from which final cross-sections are obtained:

$$\sigma_{j \rightarrow j'} = \frac{\pi}{k^2} \sum_{ll'} (2J+1) |S_{jl \rightarrow j'l'}|^2. \quad (4)$$

l is the orbital angular momentum of the relative motion, k is the wavevector, j is the rotational angular momentum.

Since the energy sudden approximation has been employed, only cross-sections out of the ground rotational states need to be calculated and the following formula

$$\sigma_{j \rightarrow j'} = (2j' + 1) \left(\frac{k_0}{k_j} \right)^2 \sum_{j''} \begin{pmatrix} j' & j & j'' \\ 0 & 0 & 0 \end{pmatrix}^2 \sigma_{0 \rightarrow j''} \quad (5)$$

is then used to trivially calculate the others with the usual meaning of the various parameters. By the very nature of the energy sudden approximation, there is an ambiguity as to which kinetic energy (entrance or exit channel) should be chosen for a particular cross-section. This problem has often been discussed. Its importance increases with the relative importance of the inelasticity as compared to the total collision energy. Following the suggestion of Chang et al. (1984), Chapman & Green (1984) showed by considering the case of $0 \rightarrow j$ rate constants for rotational excitation of CO by Ar that it is more appropriate to interpret the sudden energy as the final kinetic energy. We performed the calculations with this assumption by using a R -matrix propagator method (Kirkpatrick 1983). For exothermic reactions:

$$\sigma_{j_i \rightarrow j_f}(e) = (2j_f + 1) \sum_l (2l + 1) \begin{pmatrix} j_i & j_f & l \\ 0 & 0 & 0 \end{pmatrix}^2 \sigma_{l \rightarrow 0}(e). \quad (6)$$

We obtain $\sigma_{j_f \rightarrow j_i}$ from the microscopic reversibility condition:

$$(2j_i + 1) k_{j_i}^2 \sigma_{j_i \rightarrow j_f} = (2j_f + 1) k_{j_f}^2 \sigma_{j_f \rightarrow j_i}. \quad (7)$$

The rate constants are subsequently obtained after performing the maxwellian average over v $\sigma(v)$.

Table 2 gives the corresponding results for different temperatures relevant for interstellar conditions. We only give here the deexcitation coefficient corresponding to $\Delta j = 2$ because in homopolar C₂, odd j levels cannot exist. The IOS approximation is valid when the relative translational energy is large compared with the spacing of the rotational levels. The rotational constant of C₂ being equal to 2.618 K, this condition forces to limit the rate coefficient calculations to the transition $8 \rightarrow 6$ for $T = 100$ K. The corresponding values are about one order of magnitude smaller than for CO deexcitation by para H₂ (Flower & Launay 1985); this is ascribed to the differences in the potential energy surfaces.

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