

PROBING WEAKLY-BOUND SPECIES WITH NONRESONANT LIGHT: DISSOCIATION OF He₂ INDUCED BY ROTATIONAL HYBRIDIZATION

Bretislav FRIEDRICH¹, Manish GUPTA² and Dudley HERSCHBACH³

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford St., Cambridge, MA 02138, U.S.A.; e-mail: ¹ brich@chemistry.harvard.edu, ² mgupta@fas.harvard.edu, ³ hbach@chemistry.harvard.edu

Received April 6, 1998

Accepted April 9, 1998

We dedicate this paper to Professor Rudolf Zahradnik with admiration for his zestful and insightful contributions to quantum chemistry and to fostering fruitful interactions among clusters of scientists as well as molecules.

A field-dependent value of angular momentum can be imparted to a ⁴He₂ cluster by the interaction of its anisotropic polarizability with a nonresonant laser field. In this way a centrifugal term is introduced that can be tuned to a critical value sufficient to overcome the potential that binds the dimer. Due to its dependence on the internuclear distance and laser intensity, the critical angular momentum for dissociation is attained at different internuclear separations for different pulsed-laser intensities. As a result, the dependence of the dissociation probability on the laser intensity offers a means to map the potential and/or the polarizability anisotropy. A comparison with experiment thus could provide a test of either. The technique is applicable to other molecules in bound states close to the dissociation limit.

Key words: Dissociation; Induced dipole; Clusters; He-Dimer.

Definitive proof of the existence of the ⁴He₂ dimer has been provided by the elegant diffraction experiment of Schollkopf and Toennies¹. This capped a long and lively history, including extensive theoretical efforts (see refs^{2,3} and references cited therein). The accuracy required to treat the "weakest bond" still stretches current computational methods to their limits⁴. Here we note the possibility of determining the interatomic potential from the dependence of the dissociation probability of the dimer on the intensity of a pulsed nonresonant laser field.

Under field-free conditions, the He-dimer potential, $V(R)$, can only support the zero-point vibration (with an eigenenergy 1.3 mK below the dissociation limit) and the ground rotational state with $J = 0$; see Fig. 1. The centrifugal term in the effective potential

$$U(R) = V(R) + \frac{\langle J^2 \rangle \hbar^2}{2\mu R^2} \quad (1)$$

(with μ the reduced mass and R the internuclear distance) leads to dissociation for any higher rotational states. This occurs because the critical value of $\langle J^2 \rangle$ for which the effective potential can no longer support the zero-point state is only $\langle J^2 \rangle = 0.00095 \equiv \langle J^{*2} \rangle$, much smaller than $J(J+1)$ for $J \geq 1$.

However, an arbitrary value of the angular momentum can be imparted to the dimer by the interaction of its induced electric dipole moment with an external electric field, such as a nonresonant laser field. This interaction creates pendular states, hybrids of field-free rotor states, whose angular momenta reflect the strength of the interaction.

The time-averaged Hamiltonian for a linear molecule (or cluster) with polarizabilities α_{\parallel} and α_{\perp} parallel and perpendicular to the internuclear axis when subject to a nonresonant laser field of amplitude ϵ_0 is given by

$$\bar{H} = B\mathbf{J}^2 - \frac{1}{4} \epsilon_0^2 (\Delta\alpha \cos^2\theta + \alpha_{\perp}) . \quad (2)$$

Here \mathbf{J}^2 is the square of the angular momentum operator, $\Delta\alpha \equiv \alpha_{\parallel} - \alpha_{\perp}$ is the polarizability anisotropy, θ is the polar angle between the molecular axis and the direction of the electric field and

$$B(R) = \frac{\hbar^2}{2\mu R^2} . \quad (3)$$

The expectation value, $\langle B(R) \rangle$, is the rotational constant. From Eq. (2), the expectation value of the squared angular momentum is

$$\langle J^2 \rangle = \frac{E}{B} + \frac{\epsilon_0^2}{4B} [\Delta\alpha \langle \cos^2\theta \rangle + \alpha_{\perp}] \quad (4)$$

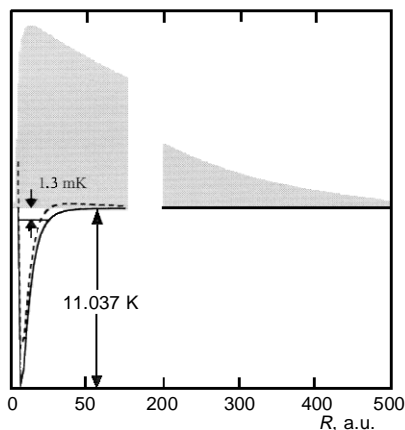


FIG. 1

Schematic view of the $^4\text{He}_2$ potential $V(R)$ (full line) and effective potential $U(R)$ (dashed) with the vibrational eigenfunction $\psi_{\text{vib}}(R)$ (shaded). The zero-point vibrational state is bound by 1.3 mK and the depth of the well, located at $R = 5.61$ a.u., is 11.037 K. The classical turning points occur at 4.996 and 26.495 a.u., respectively, and the expectation values of the internuclear distance and its square are $\langle R \rangle = 90.78$ a.u. and $\langle R^2 \rangle = 14\,509$ (a.u.)², the latter yielding a rotational constant $\langle B \rangle = 3.0$ mK

with E/B the eigenenergy and $\langle \cos^2 \theta \rangle$ the expectation value of the alignment cosine. In the low-field limit and for the ground pendular state (both pertinent here) we have⁵

$$\frac{E}{B} \approx \frac{\epsilon_0^2}{4B} \left(\frac{\Delta\alpha}{3} + \alpha_{\perp} \right) \quad (5)$$

and

$$\langle \cos^2 \theta \rangle \approx \frac{1}{3} + \frac{1}{270} \frac{\epsilon_0^2 \Delta\alpha}{B} \quad (6)$$

so that

$$\langle J^2 \rangle \approx \frac{1}{1\,080} \left(\frac{\epsilon_0^2 \Delta\alpha}{B} \right)^2. \quad (7)$$

By substituting for the polarizability anisotropy from the expansion⁶

$$\Delta\alpha = \frac{6\alpha_0^2}{R^3} + \frac{6\alpha_0^3}{R^6} \quad (8)$$

(where α_0 is the polarizability of the ground-state He atom), we can evaluate $\langle J^2 \rangle$ analytically over the whole range of internuclear separations of interest. When R exceeds 5 a.u., the second term in Eq. (8) is negligible (within 1%), so in Eq. (7) the value of $\langle J^2 \rangle$ becomes simply proportional to R .

When $\langle J^{*2} \rangle$ is reached, the dimer is aligned, with $\langle \cos^2 \theta \rangle = 0.3371$ and librates with an angular amplitude of $\approx 54^\circ$. Its spatial distribution is given by the square of a linear superposition of spherical harmonics, $Y_{J,0}$, with contributions from $J = 0$ (99.98%), $J = 2$ (0.016%) and $J = 4$ ($\approx 0.00004\%$).

The dissociation probability depends on the duration of the nonresonant laser pulse, τ_p . For a pulse duration much longer than the vibrational period (the cw limit), $\tau_p \gg \tau_v$, the molecule will vibrate through the whole range of internuclear separations. At a laser intensity sufficient to impart $\langle J^{*2} \rangle$ at any of them, the molecule will dissociate. Therefore, in the cw limit only the laser intensity corresponding to the critical angular momentum can be determined, yielding the eigenenergy but not the vibrational eigenfunction.

However, in the short pulse limit, $\tau_p \ll \tau_v$, it may be feasible to determine the vibrational eigenfunction. The critical value of angular momentum, $\langle J^{*2} \rangle$, then is reached for different field strengths (laser intensities) at different internuclear distances. At a given laser intensity, I , there is a maximum internuclear distance, R^* , up to which the dimer

receives the critical angular momentum $\langle J^{*2} \rangle$ and thus dissociates ($R^* \approx 1.62 I$ with R^* in a.u. and the laser intensity I in 10^{12} W/cm^2). In a first approximation, the probability distribution for dissociating the dimer is given by

$$F(R^*) = \int_0^{R^*} |\psi_{\text{vib}}(R)|^2 dR, \quad (9)$$

where $\psi_{\text{vib}}(R)$ is the vibrational eigenfunction. We evaluated this function by numerically solving⁷ the 1-D Schrödinger equation for $V(R)$ taken from ref.³. Figure 2 shows the dissociation probability $F(R^*)$ together with its derivative, the probability density, $f(R^*)$, as a function of R^* (and thus the laser intensity). Note that $f(R^*)$ coincides with the square of the vibrational eigenfunction.

Complicating factors include tunneling and the presence of a force exerted by the laser pulse on the dimer along its bond that tends to shorten it. This R -dependent force is due to the anisotropic polarizability; it can enhance or inhibit dissociation, depending on whether the laser pulse arrives in the contracting or stretching phase of the vibrational motion, respectively. As a result, the dissociation probability becomes a convolution of $F(R^*)$ and a function that reflects the R -dependent force. This convolution yields the dependence of R^* on the laser intensity. A full quantum mechanical analysis of the dynamics of the dissociation in the short-pulse regime is under way.

As indicated by the calculations presented here, dissociation of the helium dimer induced by rotational hybridization should be readily observable. This pertains also to

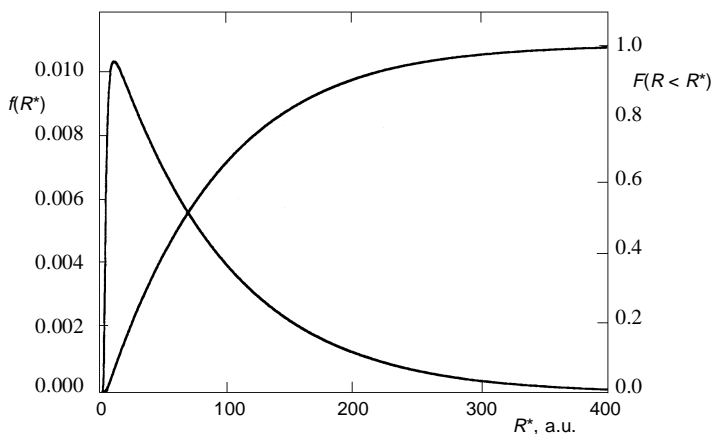


FIG. 2

The fraction $F(R < R^*)$ and its derivative $f(R^*)$ of the He_2 dimers dissociated at an internuclear distance $R < R^*$ (nonresonant induced dipole interaction). At R^* the dimer receives the critical amount of angular momentum necessary for its dissociation. Note that $f(R^*)$ coincides with the square of the zero-point vibrational eigenfunction (see text)

other feeble clusters or to ordinary molecules in vibrational states close enough to the dissociation limit. Indeed, an arbitrary value of angular momentum can be imparted to any nonspherical molecule or cluster by the interaction of its induced dipole moment with a pulsed laser field. In this way, the centrifugal repulsion can be continuously tuned to the critical value sufficient to shake off the shackles of the bond.

We are grateful for support of this work by the National Science Foundation.

REFERENCES

1. a) Schollkopf W., Toennies J. P.: *Science* **1994**, 266, 1345; b) *J. Chem. Phys.* **1996**, 104, 1155.
2. Anderson J. B., Traynor C. A., Boghosian B. M.: *J. Chem. Phys.* **1993**, 99, 345.
3. Tang K. T., Toennies J. P., Yiu C. L.: *Phys. Rev. Lett.* **1995**, 74, 1546.
4. Hobza P., Zahradnik R.: *Chem. Rev. (Washington, D.C.)* **1988**, 88, 871.
5. a) Friedrich B., Herschbach D. R.: *Phys. Rev. Lett.* **1995**, 74, 4623; b) *J. Phys. Chem.* **1995**, 99, 15686.
6. Buckingham A. D., Watts R. S.: *Mol. Phys.* **1973**, 26, 7.
7. Johnson B. R.: *J. Chem. Phys.* **1977**, 67, 4086.