

Interference in the Angular Cross Section for Photodissociation of Metastable H₂

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The anisotropy of the photodissociation cross section of metastable H₂ for excitation around the resonance due to the $j^3\Delta_g^-$ ($v=5, N=2$) level is investigated. The $j^3\Delta_g^-$ ($v=5, N=2$) state is coupled to the continuum of the $i^3\Pi_g^-$ state by the nuclear rotation. Since both states carry oscillator strength, the cross section shows interference effects. The interference is difficult to detect on the total cross section, but is clearly seen in the angular distribution of the photofragments.

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This Letter deals with the anisotropy in the photodissociation of H₂ in the metastable $c^3\Pi_u^-$ state by excitation around a resonance in the $j^3\Delta_g^-$ state, which lies in the energy range of the continuum of the $i^3\Pi_g^-$ state (see Fig. 1). This $j^3\Delta_g^-$ state gives rise to a resonance because it is predissociative, due to the coupling to the $i^3\Pi_g^-$ -state continuum by the rotational motion of the nuclei. Since both the $j^3\Delta_g^-$ and the $i^3\Pi_g^-$ state carry oscillator strength from the $c^3\Pi_u^-$ state, the photodissociation cross section as a function of energy is a Fano-Beutler profile¹ showing interference effects. Such profiles have been studied earlier in H₂ as a function of energy only.²⁻⁷ Those experimental observations, however, are restricted to measurements of the total cross section. In that case the interference between dissociation via the resonance and direct dissociation is difficult

to observe for Fano asymmetry parameters higher than 5 or 6. In the present work the differential photodissociation cross section for the first time is presented as a function of the angle of dissociation with respect to the polarization vector of the electromagnetic field. These measurements allow the direct experimental observation of interference and the determination of the relative sign of matrix elements between the states involved.

The transition moment, needed to describe the photodissociation, can be written as

$$\langle T_M \rangle = \frac{A_M(\theta)}{E - E_r + i\Gamma/2} + B_M(\theta). \quad (1)$$

This is analogous to the system treated theoretically by Mukamel and Jortner⁸ and Glass-Maujean.⁹ In Eq. (1), θ is the angle of dissociation with respect to the electromagnetic field vector, E is the photon energy, E_r is the resonant photon energy for excitation to the predissociative level with a width Γ , while M is the magnetic quantum number of the $c^3\Pi_u^-$ state corresponding to the component of the total angular momentum exclusive of spin along the electromagnetic field vector. The phase shift, corresponding to the phase factor $(E - E_r + i\Gamma/2)^{-1}$, changes over π when the photon energy is scanned over the resonance. This is due to the fact that a vibrational eigenstate is passed. It implies that the sign of the first term in Eq. (1) changes.

The first term on the right-hand side of Eq. (1) brings into account the dissociation due to excitation from the $c^3\Pi_u^-$ state to the predissociative level in the $j^3\Delta_g^-$ state. The second term corresponds to dissociation by excitation to the continuum of the $i^3\Pi_g^-$ state directly. In order to obtain the differential cross section for photodissociation into the solid angle $d\Omega = \sin(\Theta)d\Theta d\phi$, the square of the absolute value of the right-hand side of Eq. (1), multiplied by the population P_M of the corresponding rovibrational level in the $c^3\Pi_u^-$ state, has to be summed over M . As can be seen in Fig. 1, excitation to the energy range of the continuum of the $i^3\Pi_g^-$ state will also lead to excitation to the continuum of the $g^3\Sigma_g^+$ state. Since this state is not coupled to the $j^3\Delta_g^-$ state, it gives rise to a background cross section $d\sigma_g(E, \theta)/d\Omega$. The

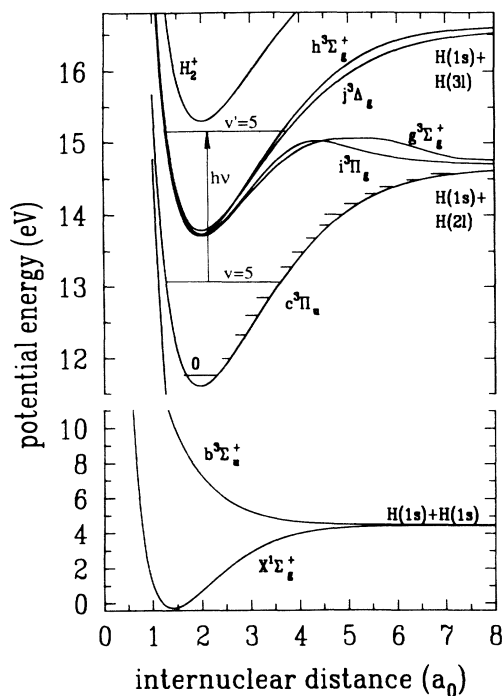


FIG. 1. Relevant potentials of H₂.

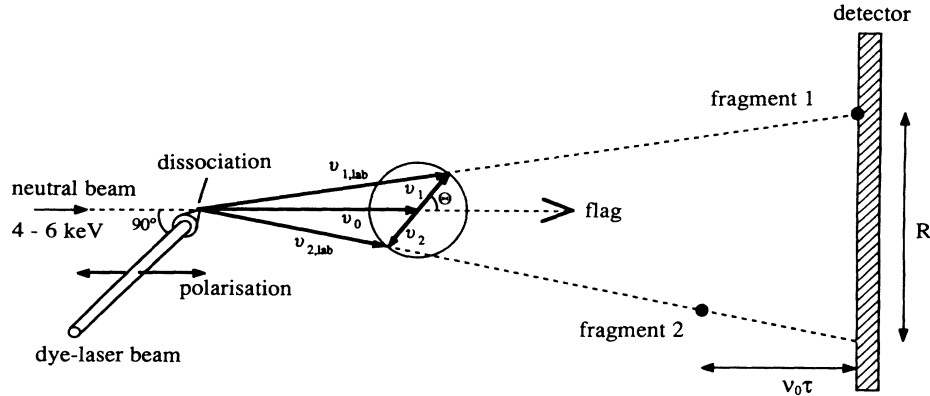


FIG. 2. Schematic representation of the experimental setup. By use of the Newton diagram, the kinetic-energy release and the dissociation angle θ can be calculated from the determined distance R and arrival-time difference τ .

differential photodissociation cross section is thus equal to

$$\begin{aligned} \frac{d\sigma(E, \theta)}{d\Omega} &= \sum_M P_M |\langle T_M \rangle|^2 + \frac{d\sigma_g(E, \theta)}{d\Omega} \\ &\equiv \frac{A(\theta)}{(E - E_r)^2 + (\Gamma/2)^2} + \frac{(E - E_r)B(\theta)}{(E - E_r)^2 + (\Gamma/2)^2} \\ &\quad + \frac{d\sigma_i(E, \theta)}{d\Omega} + \frac{d\sigma_g(E, \theta)}{d\Omega}. \end{aligned} \quad (2)$$

The first term of the last right-hand expression of Eq. (2) corresponds to excitation to the predissociative level, the second term to the interference term, and the third and fourth terms to direct excitation to the continua of the $i^3\Pi_g$ state and the $g^3\Sigma_g^+$ state, respectively. The energy range where the resonance is important is of the order of the level width Γ . Within this range the contribution of the direct excitation to the continua represented by the third and fourth terms in Eq. (2) may be considered as independent of E . The appearance of $E - E_r$ in the numerator of the interference term results in a different anisotropy for excitation below or above the resonance. It can be seen from Eq. (2) that subtraction of the cross section at $E - E_r = -\Delta E$ from that at $E - E_r = +\Delta E$ yields twice the interference term, which is equal to

$$\frac{d\sigma(E_r + \Delta E, \theta)}{d\Omega} - \frac{d\sigma(E_r - \Delta E, \theta)}{d\Omega} = \frac{2\Delta E B(\theta)}{(\Delta E)^2 + (\Gamma/2)^2}. \quad (3)$$

$B(\theta)$ can directly be obtained from the experiment by using Eq. (3).

The angular dependence of the photodissociation cross section has been measured by means of translational spectroscopy, which has proven to be an excellent tool to investigate dissociative processes.^{5,10} Both the kinetic-energy release (KER) and the angle of dissociation with respect to the molecular beam axis can be determined.

Figure 2 contains a schematic drawing of the experimental setup. The 4–6-keV beam of H_2 in the metastable $c^3\Pi_u^-$ state is created by charge exchange of H_2^+ in Cs vapor. The ions are extracted from a Nier-type electron-impact source and after mass selection with a Wien filter the H_2^+ beam is focused on the detector. The hydrogen atoms resulting from charge exchange of H_2^+ to dissociative states in H_2 are caught by a diaphragm behind the charge-exchange cell. The remaining H_2^+ ions are removed by a set of deflection plates. Behind the diaphragm the beam of H_2 in the metastable $c^3\Pi_u^-$ state is crossed by a tunable intracavity cw dye laser operated with Rhodamine-6G dye. The bandwidth of the laser is 1 cm^{-1} and its polarization vector lies along the molecular beam axis. The fragments resulting from absorption of a photon are detected in coincidence with a time- and position-sensitive detector as described in Ref. 10. The KER value ϵ in the center-of-mass system of the molecule and the angle of dissociation θ can be calculated from the determined distance R and the arrival-time difference τ of the atoms impinging on the detector. Undissociated molecules are removed by a V-shaped beam flag in order to reduce the background signal.

With an energy range of 150 to 750 meV, the KER spectra contain peaks due to excitation from several rovibrational levels in the $c^3\Pi_u^-$ state to $n=3$ Rydberg states, which decay to the $H(1s) + H(2l)$ dissociation limit. Thus the distance between the KER peaks equals the energy difference between the corresponding rovibrational levels of the $c^3\Pi_u^-$ state, which are characterized by a vibrational quantum number v and a rotational quantum number N . An example at a photon energy of 16853 cm^{-1} and a dissociation angle of 90° is shown in Fig. 3. The peaks are due to dissociation from the three lowest rotational levels belonging to $v=5$ in the $c^3\Pi_u^-$ state. The magnitude of the peak with $N=1$ clearly shows the increase of oscillator strength due to the $v'=5$, $N'=2$ resonance in the $j^3\Delta_g^-$ state. The energy of the

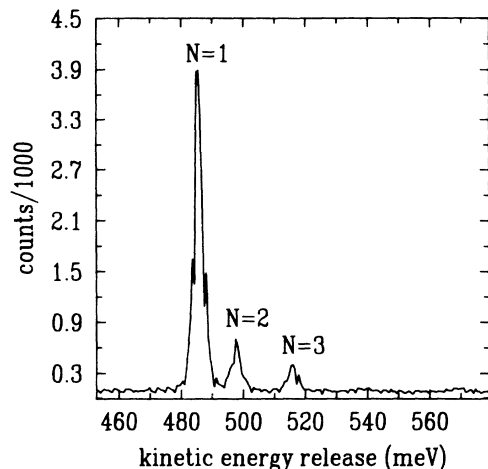


FIG. 3. Kinetic-energy release spectrum showing peaks due to photodissociation from rotational levels belonging to $v=5$ in the $c^3\Pi_u^-$ state at a photon energy of 16853 cm^{-1} and a dissociation angle of 90° .

$H(1s)+H(2l)$ dissociation limit is taken as the origin of the energy scale and so the KER is equal to the sum of the energy of the dissociated level in the $c^3\Pi_u^-$ state and the photon energy. The angular dependence of the differential photodissociation cross section $d\sigma(E,\theta)/d\Omega$ for a rovibrational level in the $c^3\Pi_u^-$ state has been obtained from the angular dependence of the number of counts N_ϵ in the corresponding peak in the KER spectrum, taken with photon energy E . If only a small fraction of the metastable molecules is dissociated, the number of counts between θ and $\theta+\Delta\theta$ can be considered directly proportional to $d\sigma(E,\theta)/d\Omega$ and is then very well approximated by

$$N_\epsilon \sim \frac{d\sigma(E,\theta)}{d\Omega} f(\epsilon,\theta) \sin\theta \Delta\theta, \quad (4)$$

where $f(\epsilon,\theta)$ is the detector efficiency for a KER value ϵ and dissociation angle θ . The detector efficiency has been determined experimentally.

The investigated resonance is the $v'=5, N'=2$ level of the $j^3\Delta_g^-$ state, which can be reached by excitation via an R branch from $v=5, N=1$ of the $c^3\Pi_u^-$ state. It has turned out from the experiments that the resonance photon energy for this transition is $16833 \pm 1\text{ cm}^{-1}$, while the level width appeared to be $23 \pm 1\text{ cm}^{-1}$. In Fig. 4 the obtained differential photodissociation cross sections are presented as a function of the dissociation angle θ for three different photon energies E . As indicated, one of the profiles in Fig. 4 is the result for a photon energy $E=16835\text{ cm}^{-1}$, which is close to the resonant excitation energy. The curves at $E=16815\text{ cm}^{-1}$ and $E=16853\text{ cm}^{-1}$ are almost one level width below and above the resonant energy, respectively. At these energies the contribution of the first term in Eq. (2) due to the resonance is about one-third of that on resonance and

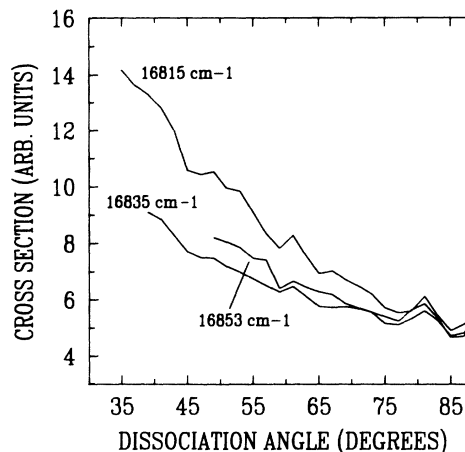


FIG. 4. Relative photodissociation cross sections obtained for $v=5, N=1$ in the $c^3\Pi_u^-$ state as a function of dissociation angle for three different photon energies. The profiles are scaled to coincide at 90° . At 16815 and 16853 cm^{-1} the magnitude of the cross section is about one-third of the one close to resonance at 16835 cm^{-1} .

the interference contribution is maximum. In order to make the comparison of their shapes easier, the angular profiles are scaled to coincide at 90° . The wiggles, which occur near the same angles in all three curves, are due to electronic crosstalk in the detector and dominate the uncertainty. The accumulated number of counts reduces the statistical error to less than 1%. The relative weak intensity of the $N=2$ peak (at most 10% for $E=16853\text{ cm}^{-1}$) ensures that the error due to partial overlap of the $N=2$ peak with the $N=1$ peak is less than 5%. It can be seen in Fig. 4 that the angular dependence of the photodissociation cross section varies as the photon energy changes. This variation is not only due to the change of the relative contribution of the first term in Eq. (2) in

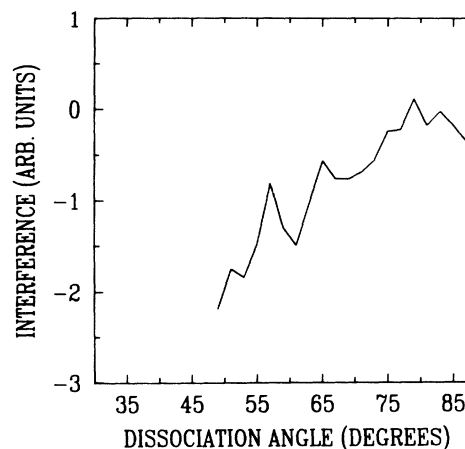


FIG. 5. Angular dependence of interference term, obtained by subtracting scaled profiles at 16815 and 16853 cm^{-1} .

comparison to the last term; the angular profiles are really different at $E = 16815$ and 16853 cm^{-1} . As can be seen from Eq. (3), subtraction of the profiles obtained at equal distance below and above the resonance gives the anisotropy of the interference term. From theory⁹ it turns out that the interference term vanishes at a dissociation angle of 90° . So, the angular profiles at equal distance from the resonance may be scaled to have the same value at 90° . The result of a subtraction of the scaled profiles at $E = 16853$ and 16815 cm^{-1} is the curve in Fig. 5. This curve shows that the interference is more important at smaller dissociation angles.

It is concluded that the anisotropy in the investigated Fano-Beutler profile, due to the $v' = 5$, $N' = 2$ resonance of the $j^3\Delta_g^-$ state, strongly exhibits interference and allows the determination of the relative sign of matrix elements.

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¹U. Fano, Phys. Rev. **124**, 1866 (1961).

²F. J. Comes and G. Schumpe, Z. Naturforsch. **26a**, 538 (1971).

³M. Glass-Maujean, J. Breton, and P. M. Guyon, Chem. Phys. Lett. **63**, 591 (1979).

⁴M. Glass-Maujean, P. M. Guyon, and J. Breton, Phys. Rev. A **33**, 346 (1986).

⁵D. P. de Bruijn and H. Helm, Phys. Rev. A **34**, 3855 (1986).

⁶J. A. Beswick and M. Glass-Maujean, Phys. Rev. A **35**, 3339 (1987).

⁷L. J. Lembo, D. L. Heustis, S. R. Keiding, N. Bjerre, and H. Helm, Phys. Rev. A **38**, 3447 (1988).

⁸S. Mukamel and J. Jortner, Chem. Phys. Lett. **29**, 169 (1974).

⁹M. Glass-Maujean (to be published).

¹⁰D. P. de Bruijn and J. Los, Rev. Sci. Instrum. **53**, 1020 (1982).