

# Determination of the transition dipole moment $\mu_{j \rightarrow b}(R)$ in $H_2$ from the measurement of vibrational wave functions

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In this work we present a theoretical and experimental study of the  $i^3\Pi_g^- \rightarrow b^3\Sigma_u^+$  transition dipole moment in molecular hydrogen. By means of translational spectroscopy the functional dependence on internuclear distance of the transition dipole moment was directly probed. Selective excitation of the  $i^3\Pi_g^-, N=1$  level, being unaffected by rotational couplings with other  $3d$  singly excited states, allows for straightforward comparison with *ab initio* calculations. Excellent agreement is found.

## I. INTRODUCTION

The  $3d$  singly excited triplet complex in molecular hydrogen is heavily affected by  $L$  uncoupling. Nuclear rotation couples nearly degenerate electronic states that differ in the projection of the electronic orbital angular momentum on the internuclear axis,  $\Lambda$ . Stated differently, the  $3d$  electron orbital is distant enough from the core that the electron cannot follow nuclear motion adiabatically. For increasing nuclear rotation the molecule-fixed quantum number  $\Lambda$  loses its meaning in favor of the laboratory-fixed quantum number  $L$ , the electronic orbital angular momentum.

*Ab initio* calculations are generally performed in the clamped nuclei approximation. Any experimental data on this triplet  $3d$  complex should therefore either be deperturbed or be taken in an exceptionally unperturbed situation. The latter is the case for the  $i^3\Pi_g^-, N=1$  state: Neither can it mix with the  $j^3\Delta_g$  state, in which the  $N=1$  rotational level is absent; nor can it be perturbed by the  $g$  and  $h^3\Sigma_g^+$  states which are of opposite parity.

By selectively exciting this ro-electronic state we determined the functional dependence on internuclear distance of the transition dipole moment to the dissociative  $b^3\Sigma_u^+$  state. We determined this functional dependence from the experimental data for four vibrational levels, which indeed yield the same transition dipole moment. These results are compared to *ab initio* calculations presented in Sec. III.

## II. EXPERIMENTAL

Translational spectroscopy has been proven an excellent means of studying the electronic structure of diatomic molecules. For simple molecules such as  $H_2$ , HeH, and  $O_2$  much work has been done recently.<sup>1-3</sup> A particularly attractive application of translational spectroscopy is the recovery of vibrational wave functions<sup>4</sup> from the experimental data, representing the eigenfunction of the nuclear Schrödinger equation rather than its energy eigenvalue, the measurement of which is common practice in spectroscopy.

As the apparatus has been described elsewhere in the

literature,<sup>5</sup> we will limit ourselves to giving a brief discussion of it. A schematic drawing is shown in Fig. 1. Hydrogenic molecular ions are formed in an electron impact ion source, accelerated to an energy  $E_0 = 6800$  eV, mass analyzed and finally charge exchanged on cesium vapor. The remaining ions are bent away by a static electric field. Fragments from short-lived molecular states scatter out of the beam and are removed by a diaphragm. This way a neutral beam is obtained in the metastable  $c^3\Pi_u^-$  state. Rovibrational levels of the  $i^3\Pi_g^-$  state are selectively excited with a dye laser, and dissociate after photon emission. After a flight length of one meter the fragments are detected with a position and time sensitive detector.<sup>6</sup> Intact molecules are intercepted by a beam flag to reduce the background signal from metastable decay and collision induced dissociations. The kinetic energy released in the dissociation process is deduced from the fragment positions at short time differences ( $\tau < 2$  ns; i.e. dissociation angle  $\theta = 90^\circ$ ).

The relation between vibrational wave function in the excited level and the kinetic energy release (KER) is visualized in Fig. 2. The excited  $i^3\Pi_g^-$  state decays to the dissociative  $b^3\Sigma_u^+$  state by photon emission, indicated by the vertical lines. Photon energy and released kinetic energy add up to the excited state potential energy with respect to the  $b^3\Sigma_u^+$  state dissociation limit. For this experiment our technique combines three advantages with respect to fluorescence photon detection. First, the required dynamic range in energy is much more easily covered. Second, our solid angle of detection approaches  $4\pi$ . Third, we simultaneously observe all KER values, thereby eliminating errors arising from laser or molecular beam instabilities.

Within the Born-Oppenheimer approximation transformation of a KER spectrum to a product of vibrational wave function and electronic transition dipole moment is possible. This is accomplished using the completeness of the continuum vibrational wave functions  $\chi_\epsilon(R)$  in the repulsive  $b^3\Sigma_u^+$  state as described by Koot *et al.*<sup>4</sup> Accordingly we obtain

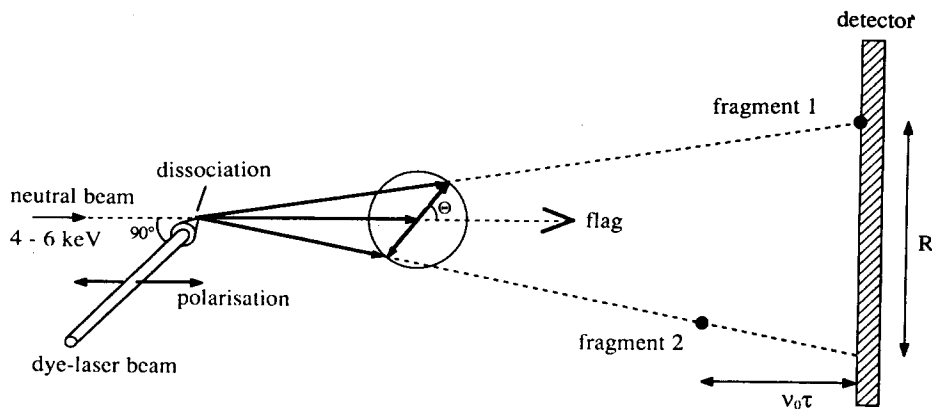


FIG. 1. Schematic experimental setup. The released kinetic energy is determined as  $\epsilon = E_0(R/2L)^2$ , with beam energy  $E_0 = 6800$  eV, flight length  $L = 1$  m.

$$\mu(R)\xi(R) = \int_0^\infty [N(\epsilon)\nu_\epsilon^{-3}]^{1/2}\chi_\epsilon(R)d\epsilon$$

with  $R$  the distance between the nuclei,  $\mu(R)$  the transition dipole moment between the electronic states,  $\xi(R)$  the bound vibrational wave function,  $\epsilon$  the released kinetic energy,  $\chi_\epsilon(R)$  the continuum vibrational wave function,  $N(\epsilon)$  the intensity (number of counts) at energy  $\epsilon$  in the KER spectrum, and  $\nu_\epsilon$  the frequency of the emitted photon. Since the  $b^3\Sigma_u^+$  potential curve is very accurately known,<sup>7</sup> one can calculate the  $\chi_\epsilon(R)$  continuum vibrational wave functions and perform the integration to obtain the product of transition dipole moment and bound vibrational wave function. This product is finally divided by the bound vibrational wave function, calculated using the highly accurate Born–Oppen-

heimer potential curve of the  $i^3\Pi_g$  state,<sup>8</sup> thus yielding the  $R$  dependence of the transition dipole moment.

### III. *AB INITIO* THEORETICAL CALCULATION OF THE ELECTRONIC TRANSITION DIPOLE MOMENT FUNCTION

The theoretical prediction of the  $R$  dependence of the electronic transition dipole moment is obtained from calculating the residues of the nonrelativistic multiconfigurational linear response function (MCLR).<sup>9,10</sup> The multiconfigurational self-consistent field (MCSCF) wave functions were determined using the SIRIUS MCSCF program<sup>11</sup> and the subsequent calculation of the transition dipole moment was carried out using the MCLR program of Jørgensen *et al.*<sup>10</sup> Two different basis sets were applied because of linear dependence among the basis functions for small internuclear distances. For  $R \in [2.0; 3.7]$  we used the basis set *A* 40 of Augspurger and Dykstra<sup>12</sup> with all orbitals uncontracted and for  $R \in [1.4; 1.8]$  the most diffuse *s* orbital was moved to the center of mass. The MCSCF wave function for the  $b^3\Sigma_u^+$  state was calculated for the complete active space (CAS)  $[1\sigma_g^+ 2\sigma_g^+ 3\sigma_g^+ 1\pi_g 1\pi_u 1\sigma_g^+ 2\sigma_g^+ 3\sigma_g^+]$  including both electrons in the CAS. In Table I we report the MCLR excitation energy, dipole length and dipole velocity oscillator strengths, and transition dipole moment for the  $i^3\Pi_g^- \rightarrow b^3\Sigma_u^+$  transition at 23 different internuclear distances. The oscillator strengths were calculated in the dipole length and dipole velocity gauge to obtain a check on the completeness of the basis set, as the two oscillator strengths become equal in a complete basis. The oscillator strengths in Table I differ at most 1% suggesting the calculated transition dipole moments are correct within 1%.

The value of the transition dipole moment as a function of  $R$  is determined by the changes in the two wave functions involved. For  $R \rightarrow 0$  it approaches the united atom limit of  $1.880 ea_0$ .<sup>13</sup> When  $0 < R < R_c$  the fast decrease is given by the rapid configurational change in the  $b^3\Sigma_u^+$  electronic wave function from a  $2p$ -like united-atom orbital into the ungerade linear combination of two  $1s$  hydrogenic orbitals, which have a small overlap with the  $3d$ -like  $i^3\Pi_g^-$  state. At larger  $R$  the value increases again because the  $i^3\Pi_g^-$  state changes in the barrier region: It becomes  $2p$ -like, whereby the overlap to the  $b^3\Sigma_u^+$  state improves again. The separated atom limit is  $0.745 ea_0$ .<sup>13</sup>

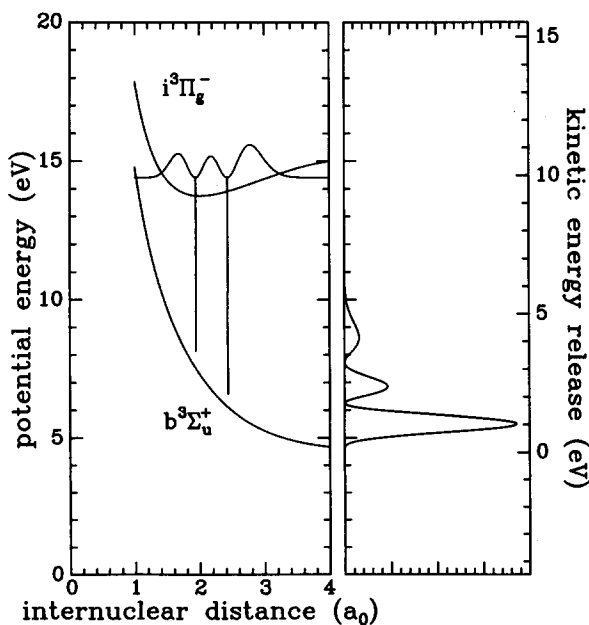


FIG. 2. Potential energy diagram showing the  $b^3\Sigma_u^+$  and  $i^3\Pi_g^-$  states in H<sub>2</sub>. Zero potential energy is defined as the molecular ground state level. Fluorescence from the excited  $i^3\Pi_g^-$  state to the dissociative  $b^3\Sigma_u^+$  state gives rise to a kinetic energy release spectrum reflecting the bound wave function.

TABLE I. *Ab initio* calculated MCLR excitation energies, dipole length and dipole velocity oscillator strengths, and transition dipole moments for the  $i^3\Pi_g^- \rightarrow b^3\Sigma_u^+$  transition in molecular hydrogen.

$R(a_0)$	$\Delta E_e$ (eV)	$f^l$ ( $10^{-2}$ )	$f^v$ ( $10^{-2}$ )	$ \mu $ ( $ea_0$ )
1.4	4.303	6.50	6.47	0.785
1.5	4.658	5.77	5.73	0.711
1.6	5.024	5.17	5.14	0.648
1.7	5.394	4.69	4.66	0.596
1.8	5.763	4.31	4.29	0.553
2.0	6.478	3.82	3.80	0.491
2.1	6.818	3.69	3.66	0.469
2.2	7.143	3.60	3.58	0.454
2.3	7.451	3.56	3.54	0.442
2.4	7.743	3.57	3.55	0.434
2.5	8.017	3.63	3.62	0.430
2.6	8.275	3.72	3.71	0.429
2.7	8.516	3.87	3.86	0.431
2.8	8.742	4.06	4.05	0.435
2.9	8.952	4.27	4.26	0.441
3.0	9.147	4.56	4.54	0.451
3.1	9.328	4.93	4.91	0.464
3.2	9.495	5.38	5.36	0.481
3.3	9.649	5.94	5.92	0.501
3.4	9.790	6.61	6.59	0.525
3.5	9.918	7.43	7.41	0.553
3.6	10.034	8.42	8.40	0.585
3.7	10.147	9.59	9.57	0.621

#### IV. RESULTS AND DISCUSSION

We measured KER spectra of the vibrational levels  $v = 0, 1, 2$ , and 3. For  $v = 1$  the  $P2$  transition could not be resolved from the  $P4$  transition, their difference being one hundredth of our laser bandwidth ( $1 \text{ cm}^{-1}$ ). In our ion source the  $N = 4$  level is, however, much less populated than the  $N = 2$  level, and good results could be obtained.

After subtraction of background due to collision induced dissociations and metastable decay the spectra still show a background, induced by the laser. This contribution is subtracted by measuring KER spectra  $3 \text{ cm}^{-1}$  off resonance. This laser induced background originates from transitions to other dissociative states. The accuracy of the final result is mainly determined by the subtraction procedure.

A spectrum for the  $v = 2$  vibrational level is shown in Fig. 3. For an  $R$  independent transition dipole moment the number of zeroes in the KER spectrum is equal to the number of nodes of the bound vibrational wave function. The observation of two nodes (at  $\epsilon = 1.8$  and  $3.3$  eV approximately) implies that the transition dipole moment has no node in the internuclear distance region where the vibrational wave function has significant amplitude. The spectra have been transformed using the closure relation as described above. Division of the transformed spectra by the theoretical wave functions calculated from a Born–Oppenheimer potential curve for the  $i^3\Pi_g^-$  state<sup>8</sup> yields the experimental  $R$  dependence of the transition dipole moment (Fig. 4). The spikes result from division around the nodes of the wave function, and are interpolated in the final result, Fig. 5. The experimental curves were scaled to the *ab initio* theoretical curve, since this experiment does not yield absolute values for the transition dipole moment.

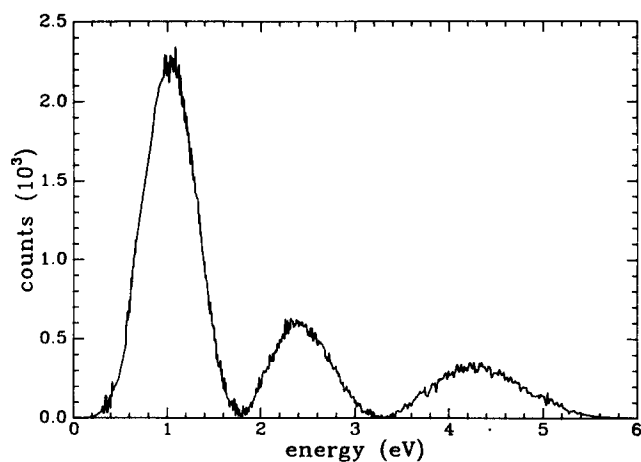


FIG. 3. Kinetic energy release spectrum obtained from the  $v = 2, N = 1$  level of the  $i^3\Pi_g^-$  state after background subtraction (see text) and removal of a sharp superimposed peak around 0.4 eV due to resonant excitation of a predissociative level.

Since higher vibrational wave functions reach out farther from the equilibrium distance, the experimental data for the dipole moment have distinct intervals of reliability: Only the  $v = 3$  curve convincingly penetrates the region at long internuclear distances where the absolute value of the transition dipole moment increases again. The data taken from earlier measurements by Koot *et al.*<sup>14</sup> were calculated from the maxima of the wave functions only, and therefore give rise to discrete values of the dipole moment. It should be noticed that their experiments were done on partially perturbed excited states. Figure 5 however shows that there is good agreement with the theoretical curve; this means that the perturbation of the  $h^3\Sigma_g^+, g^3\Sigma_g^+$ , and  $j^3\Delta_g$  states does not substantially alter the radiative behavior of the  $i^3\Pi_g^-$  state. This can be understood by considering the perturbed  $i$  state as a superposition of the unperturbed states:<sup>15</sup>

$$|i\rangle_{\text{perturbed}} = c_g |g\rangle + c_h |h\rangle + c_i |i\rangle + c_j |j\rangle.$$

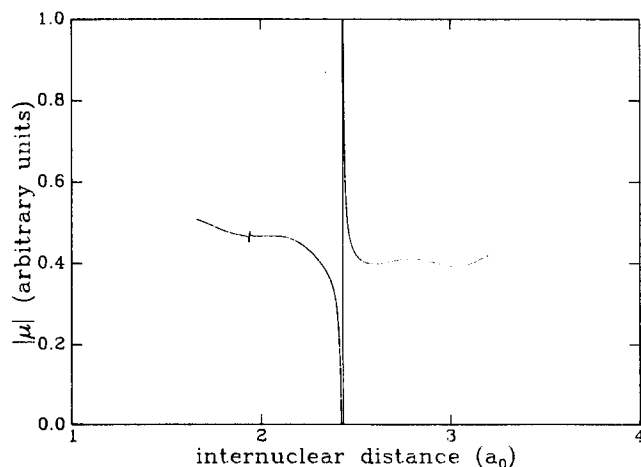


FIG. 4. Plot of the electronic transition dipole moment as obtained from the experimental and theoretical data for the  $v = 2, N = 1$  level of the  $i^3\Pi_g^-$  state. The spikes reflect the wave function's nodes.

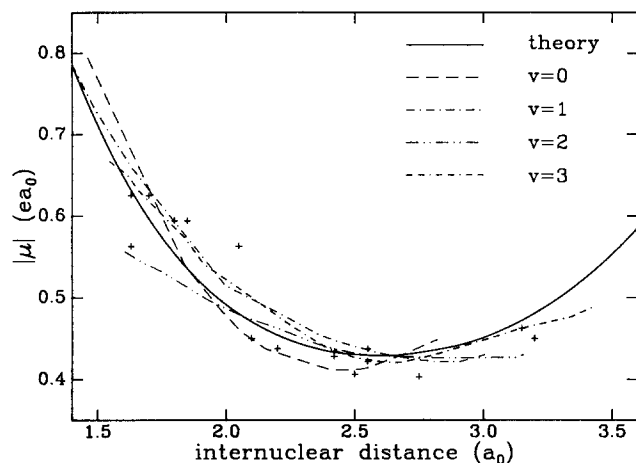


FIG. 5. Combined plot of the experimental and theoretical transition dipole data for the  $i^3\Pi_g^- \rightarrow b^3\Sigma_u^+$  transition in molecular hydrogen. The theoretical curve is represented by the continuous line. The single observations (+) are taken from the work of Koot *et al.*,<sup>14</sup> and were determined at the wave functions' maxima only. The four noncontinuous curves represent the experimental data, and are labeled by the vibrational quantum numbers of the initial  $i^3\Pi_g^-$  state.

The  $|j\rangle$  state contribution has no direct influence since its radiation to the  $b^3\Sigma_u^+$  state is dipole forbidden; the  $|h\rangle$  state contribution is assumed to be small, since it can perturb the  $i^3\Pi_g^-$  state only via the  $g^3\Sigma_g^+$  state;<sup>15</sup> but the  $|g\rangle$  state surely contributes. Hence we must conclude that the  $|g\rangle \rightarrow b^3\Sigma_u^+$  transition dipole moment is quite similar to the  $|i\rangle \rightarrow b^3\Sigma_u^+$  transition dipole moment. A study on the radiative decay of the  $g$  and  $h^3\Sigma_g^+$  states qualitatively confirms this, as will be reported elsewhere.<sup>16</sup>

Radiative decay to a dissociative potential offers all the information needed to recover the dependence on internuclear distance of the transition dipole moment, via the measurement of vibrational wave functions. Our experimental technique has confirmed, with a high level of accuracy, the *ab initio* results, which point out a substantial change of the transition dipole moment over a small range of internuclear separation.

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<sup>15</sup>For the  $i^3\Pi_g^-$  and  $j^3\Delta_g^-$  states these unperturbed states are the Born-Oppenheimer states, as directly obtained by the *ab initio* calculations. For the  $g^3\Sigma_g^+$  and  $h^3\Sigma_g^+$  states the situation is different. Experimental data for the  $g^3\Sigma_g^+$  state (see Ref. 14) seem to indicate an overall 3d electronic character, while *ab initio* calculations [see, e.g., J. Rychlewski, *Phys. Rev. Lett.* **63**, 1223 (1989) on the  $h^3\Sigma_g^+$  state] predict a sudden change from 3d to 3s electronic character at equilibrium. We prefer the diabatic picture since it agrees better with the experimental data. According to this picture the  $g^3\Sigma_g^+$  state behaves 3d-like, and the  $h^3\Sigma_g^+$  state 3s-like for all internuclear separations. The 3s  $h^3\Sigma_g^+$  state can perturb the 3d  $g^3\Sigma_g^+$  state via vibrational motion. The 3d  $g^3\Sigma_g^+$  state can perturb the 3d  $i^3\Pi_g^-$  state via L uncoupling.

<sup>16</sup>J. M. Schins, L. D. A. Siebbeles, W. J. van der Zande, J. Los, and J. Rychlewski (unpublished).