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# Perturbations in the $b^4\Sigma_g^-$ state of $O_2{}^+$ immediately below the predissociation limit, studied by high-resolution optical-optical double-resonance photofragment spectroscopy

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Optical-optical double-resonance photofragment spectroscopy of molecular ions is, for the first time, performed with a Doppler-limited resolution of 0.003 $\text{cm}^{-1}$. The high resolution allows the observation of perturbations in the $b^4\Sigma_g^-$ state arising from a vibrationally excited level in the $d^4\Sigma_g^+$ state lying only 29 $\text{cm}^{-1}$ below the predissociation limit. The matrix element for the interaction between the $b$ and $d$ states is obtained from a perturbation analysis and is used to estimate the contribution of the $d$ state to the predissociation of the $b$ state. Precise effective Hamiltonians are reported for the $a^4\Pi_u(v''=4,5)$ and $b^4\Sigma_g^-(v'=4)$ states.

## INTRODUCTION

The predissociation of the $O_2{}^+$ ion in the $b^4\Sigma_g^-$ state has been the subject of numerous investigations by laser photofragment spectroscopy. The rotational and electronic fine structure has been studied under high resolution,[1,2] the energies and angular distributions of the $O^+$ photofragments have been analyzed,[3,4] and the linewidths of the predissociating levels have been interpreted in terms of perturbations from the continuum part of electronic states that correlate to the lowest dissociation limit; $O^+(^4S^o)+O(^3P_2)$.[5–8] A problem in the analysis of the linewidths is the lack of spectroscopic observations of some of the electronic states assumed to be important in the predissociation mechanism.

The interactions that give rise to predissociation above the dissociation limit may cause significant perturbations of the energy levels below the dissociation limit in case of near degeneracy of two discrete levels of different electronic states. Such degeneracies are particularly likely to occur immediately below the dissociation limit where the density of discrete states is high. $O_2{}^+$ offers a very good opportunity to investigate the behavior of an electronic state across the dissociation limit: The state $b^4\Sigma_g^-(v'=4)$ has levels above as well as below the dissociation limit, with the lowest predissociating level lying only 14.2 $\text{cm}^{-1}$ above the limit.[4]

Recently, Cosby and Helm[9] introduced the technique of optical-optical double-resonance (OODR) photofragment spectroscopy, which allows the study of levels below the dissociation limit while preserving the high sensitivity of the photofragment detection scheme. Furthermore, the OODR technique provides a unique labeling of the lower level, so that the energy levels of the upper state are determined unambiguously. This paper is the first report of OODR photofragment spectroscopy carried out with a Doppler-limited resolution of 0.003 $\text{cm}^{-1}$.

## EXPERIMENTAL

The apparatus used in the photofragment experiments is shown in Fig. 1. $O_2{}^+$ ions formed in a radiofrequency discharge in $O_2$ gas are accelerated to 40—50 keV and mass selected before they enter the 3-m-long collinear interaction region. The interaction region is divided into a "pump region" which is on ground electrostatic potential, and a "probe region" which can be separately Doppler tuned by applying a post-acceleration voltage to a Faraday cage. The $O^+$ ions formed in the interaction region are deflected and decelerated down to $\sim 10\%$ of their kinetic energy before they enter a hemispherical electrostatic analyzer and finally are detected with a channeltron detector. The combination of the retardation and the hemispherical analyzer has an energy resolution of $3\times10^{-4}$, which allows separation of the $O^+$ fragments from the two parts of the interaction region.

The two single-mode dye lasers were operated with bandwidths smaller than 1 MHz and output powers of 200 mW for the pump laser and 70 mW for the probe laser. The wavelengths of the two lasers were measured with a relative precision of $10^{-8}$ by means of a $\lambda$ meter with a thermally stabilized He-Ne reference laser, calibrated absolutely to within $10^{-7}$ against the iodine

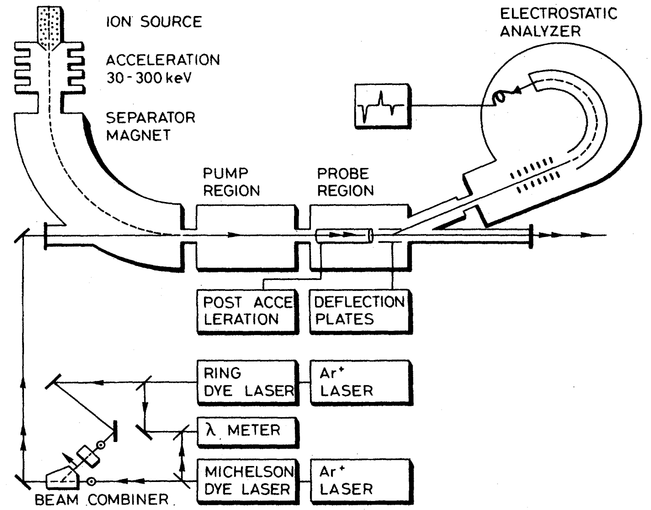

FIG. 1. Experimental setup for optical-optical double-resonance photofragment spectroscopy.

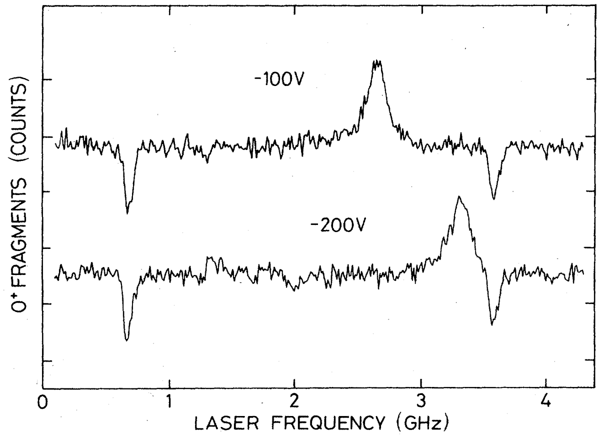

FIG. 2. Optical-optical double resonances probed on the transition $b^4\Sigma_g^-(v'=4,\ J=8.5,\ N=9)\leftarrow a^4\Pi_u(v''=5,\ J=8.5,\ \Omega=\frac{5}{2})$ at two different post-acceleration voltages. The double resonances (dips) are transitions to the perturbed levels $(J)_N=(7.5)_7$ and $(7.5)_8$ of $b^4\Sigma_g^-$ and $d^4\Sigma_g^+$, respectively. The peak is the predissociating transition $b\ (v'=4,\ J=18.5,\ N=17)\leftarrow a\ (v''=5,\ J=17.5,\ \Omega=\frac{3}{2})$ induced by the pump laser in the probe region.

fluorescence spectrum. The beams of the two lasers were merged by turning the polarization of the pump laser by 90° and combining the two beams in a Glan-Thomson prism. The laser beams were focused down to 2 mm in the interaction region.

The OODR experiments were carried out by keeping the probe laser fixed on resonance with a transition from the $a^4\Pi_u(v''=5)$ state to a predissociating level in the $b^4\Sigma_g^-(v'=4)$ state in the probe region and tuning the pump laser across transitions from the same lower level. When the pump laser comes into resonance with such a transition in the pump region, it depletes the population in the lower level, which results in a decrease in the signal from the probe region. By accidence, the pump laser may be tuned into resonance with a transition to a predissociating level in the probe region, thus giving rise to an increase in the number of $O^+$ fragments detected. Figure 2 shows two double resonances and a resonance with a predissociating transition in the probe region. The latter is Doppler-shifted when the post-acceleration voltage is changed while the double resonances remain fixed.

## RESULTS AND DISCUSSION

As a basis for the OODR experiments, we measured the wavelengths of more than 200 transitions to the predissociating levels of $b^4\Sigma_g^-(v'=4,\ N\geq 9)$ from $a^4\Pi_u(v''=4{,}5)$ using only one laser. For each of the two bands, a standard ion velocity was selected so that one transition was in resonance with the laser running parallel to the ions, while a second transition was in resonance with the same laser beam running in the opposite direction. The Doppler factor applying to all measurements at this standard velocity was determined with an accuracy of $3\times 10^{-8}$ by measuring several transitions for both directions of the laser beam. The fine-structure splittings of the $b^4\Sigma_g^-(v'=4,\ N=9{,}11{,}13)$ levels were measured by means of a calibrated Fabry-Perot interferometer, yielding a precision three times better than that obtained with the $\lambda$ meter.

The data were used in a least-squares fit to determine the parameters in the effective spin-rotational Hamiltonians of Zare *et al.*,[10] including the third-order spin-orbit term of Brown *et al.*[11] The standard errors obtained here are generally smaller than those of previous measurements,[1,2] so that the values of all of the spectroscopic parameters are now well defined on the 99% confidence level. The fit reproduces the measured wave numbers with a standard deviation of 0.0015 $\text{cm}^{-1}$ (Table I).

Transitions to levels above the dissociation limit in $b^4\Sigma_g^-(v'=4)$ have natural linewidths of 190—500 MHz due to the predissociation.[7] The Doppler width arising from the velocity spread in the ion beam is only ~80 MHz, implying that a single frequency laser in resonance

TABLE I. Parameters (values in $\text{cm}^{-1}$ followed by one standard error on the last digits) of the effective Hamiltonians for $a^4\Pi_u(v''=4{,}5)$ and $b^4\Sigma_g^-(v'=4)$ determined from transitions to the predissociating ($N\geq 9$) levels in the $b$ state.

| | $a(v''=4)$ | $a(v''=5)$ | $b(v'=4)$ |
|---|---|---|---|
| $T$ | −17 177.073 2(10)[a] | −16 245.412 8(10)[a] | ≡0 |
| $B$ | 1.034 886 5(42) | 1.019 164 0(53) | 1.186 398 1(21) |
| $10^6D$ | 5.129(9) | 5.157(13) | 6.507(9) |
| $\epsilon$ | 0.623 92(22) | 0.626 65(21) | 0.139 213(71) |
| $10^3\gamma$ | −4.05(33) | −3.61(34) | −1.256(9) |
| $A$ | −47.704 93(51) | −47.638 37(48) | |
| $10^5A_D$ | 5.9(13) | 5.2(14) | |
| $\eta$ | 0.053 97(47) | 0.054 78(48) | |
| $\alpha$ | 0.198 91(33) | 0.222 68(39) | |
| $10^3p$ | 4.298(31) | 4.336(35) | |
| $10^5q$ | −2.28(32) | −2.72(35) | |

$\sigma=0.0015\ \text{cm}^{-1}$

[a] These values have an additional uncertainty of 0.0025 $\text{cm}^{-1}$ arising from the absolute calibration of the wavelengths.

with a predissociating transition interacts with all velocity classes in the beam. However, the efficiency of the optical pumping is lowered because the oscillator strength of the transition is "spread out" over the natural line shape. Transitions to levels below the dissociation limit have natural linewidths much smaller than the Doppler width. Therefore, optical pumping is very efficient in this case but occurs only in a single velocity class. This limits the strength of the OODR photofragment signal, since the probe laser necessarily interacts with all velocity classes on a transition to a predissociating level. This implies, furthermore, that the resolution of OODR photofragment spectra is Doppler limited, in contrast to OODR detected on fluorescence from long-lived levels, which is Doppler free to first order. In the most favorable cases, we obtained a 25% reduction in the probe signal by pumping on transitions to levels below the dissociation limit. This rather efficient optical pumping suggests that there is some power broadening of the bound-bound transitions induced by the pump laser.

In the present study, we observed those six bound levels in the $b^4\Sigma_g^-(v'=4)$ state which are accessible by OODR probed on transitions to predissociating levels in that vibrational state. Furthermore, we observed two levels from a perturbing state that are almost degenerate with levels in the $b$ state. Most of the levels were observed by pumping from two different levels in the $a^4\Pi_u(v''=5)$ state, thus providing a double check of the measured wave numbers and a confirmation of the $J$ values assigned to the levels. The term values of the observed levels are listed in Table II along with their deviations from those calculated from the effective Hamiltonian representing the predissociating levels of the $b$ state. All except one of the measured levels in the $b$ state deviate by more than three standard deviations (0.0045 $\text{cm}^{-1}$) from the calculated term values, indicating perturbations from other electronic states. The largest perturbations occur in the $b$ $(J)_N=(8.5)_7$, $(7.5)_7$, and $(6.5)_7$ levels; two other levels with $J=7.5$ and 6.5 appear as extra lines in the OODR spectra (Fig. 2), and it seems obvious that these levels are responsible for the perturbations of the $(7.5)_7$ and $(6.5)_7$ levels in the $b$ state.

The electronic state that perturbs three of the $b$ $(N=7)$ levels must have closely spaced levels at the three adjacent $J$ values. For electronic states with nonzero electronic orbital angular momentum $(\Pi,\Delta,\ldots)$ this would require an unreasonably small rotational constant, whereas $\Sigma$ states will have $(2S+1)$ closely spaced fine-structure levels. Accordingly, the perturbations in the $b$ state must arise from a $\Sigma_g$ state with spin multiplicity $\geq 4$, and the only such state with levels expected below the lowest dissociation limit is $d^4\Sigma_g^+$. For reasons of nuclear symmetry, this state has only even $N$ levels in $^{16,16}O_2{}^+$. Accordingly, we attribute the strong perturbations of the $b$ $(8.5)_7$, $(7.5)_7$, and $(6.5)_7$ levels to interactions with the $d$ $(8.5)_8$, $(7.5)_8$, and $(6.5)_8$ levels in a vibrational state immediately below the dissociation limit. To our knowledge, this is the first spectroscopic observation of bound levels in the $d^4\Sigma_g^+$ state of $O_2{}^+$. The transition moment for $d^4\Sigma_g^+\leftarrow a^4\Pi_u$ is very small,[8] but becomes large in the $(7.5)_8$ and $(6.5)_8$ levels because of the mixing with the $(7.5)_7$ and $(6.5)_7$ levels of the $b$ state.

TABLE II. Levels below the dissociation limit observed by OODR.

| State | $J$ | $N$ | Term value[a] | Observed-Calculated |
|---|---|---|---|---|
| $b$ | 8.5 | 7 | 66.2137 | −0.0155 |
| $b$ | 7.5 | 7 | 66.6087 | −0.0495 |
| $d$ | 7.5 | 8 | 66.7386 | |
| $b$ | 6.5 | 7 | 66.5378 | −0.0525 |
| $d$ | 6.5 | 8 | 66.6634 | |
| $b$ | 5.5 | 7 | 66.1851 | 0.0052 |
| $b$ | 6.5 | 5 | 35.4113 | 0.0000 |
| $b$ | 5.5 | 5 | 35.8336 | −0.0047 |

[a] Values in $\text{cm}^{-1}$ relative to the term origin of $b^4\Sigma_g^-(v'=4)$.

The observation of perturbed levels from both electronic states allows us to derive the term values for the corresponding unperturbed levels, as well as two values for the reduced matrix element, $\tau$, between the $b$ and $d$ states in the vibrational levels in question. Using the angular factors of Kovács,[12] we obtain $\tau$ values of 0.23 and 0.19 $\text{cm}^{-1}$ for $J=6.5$ and 7.5, respectively. Assuming that the small perturbation of the $b$ $(5.5)_7$ level arises from interaction with $d$ $(5.5)_6$, we find that the latter level lies 1.1 $\text{cm}^{-1}$ below the unperturbed $d$ $(7.5)_8$ level, implying that the perturbing vibrational level of the $d$ state has an effective rotational constant of 0.04 $\text{cm}^{-1}$, and a term origin which lies 3 $\text{cm}^{-1}$ below $b$ $(7.5)_7$ or 29 $\text{cm}^{-1}$ below the dissociation limit, $O^+(^4S^o)+O(^3P_2)$.

Assuming constant Franck-Condon overlap, the matrix element for the interaction between the $b$ and $d$ states may be used for estimating the contribution from the continuum part of the $d$ state to the predissociation widths of the $(v'=4,\ N\geq 9)$ levels of the $b$ state:[13]

$$\Gamma_{bd}(J,N)=2\pi(dv/dE)\tau^2\sum_{N'}\chi_{JNN'}^2\ , \tag{1}$$

where $(dv/dE)$ is the density of vibrational levels in the $d$ state around the level which gives rise to the perturbation, and $\chi_{JNN'}$ are the angular factors for the $\Sigma^+,\Sigma^-$ interaction.

The only unknown parameter is the density of levels, which for states close to the dissociation limit to a good approximation can be described in terms of the long-range part of the potential. For potentials of the form

$$V(R)=D-C_n/R^n\ , \tag{2}$$

where $R$ is the internuclear distance, the spacing between vibrational levels is[14]

$$dE/dv=K_n(D-E)^{(n+2)/2n}\ , \tag{3}$$

where $K_n$ is a constant which depends on $n$, $C_n$, and the reduced mass of the molecule.

According to the theoretical treatment by Gentry and Giese,[15] the long-range interaction between $O(^3P)$ and an ion has charge-quadrupole $(R^{-3})$ as well as charge-induced dipole $(R^{-4})$ contributions. At the separations of interest in the present study, both terms contribute significantly, so we adopt an "effective" exponent,[14] $n=3.5$, which gives a very good representation of the "true" potential function[15] in the range 7—10 Å. Inserting the experimental values of $\tau$ and $E$ in Eqs. (1) and (3) we obtain a vibrational spacing of 8 $\text{cm}^{-1}$ and a width of 90 MHz for the $J=N\pm\frac{3}{2}$ levels of the $b\,^4\Sigma_g^-(v'=4)$ state, which is significantly smaller than the experimental widths of 190—250 MHz.[7] This discrepancy may arise from the model for the long-range potential but may also be taken as an indication that states other than $d\,^4\Sigma_g^+$ contribute significantly to the predissociation of the $b\,(v'=4)$ state.

In general, there will be a high density of levels immediately below the dissociation limit of a molecule, which suggests that perturbations similar to those described here are likely to occur in other predissociating molecules as well. This has previously been considered for predissociation and perturbations in $N_2^+$.[16] The combined observation of perturbations and predissociation that can be obtained with high resolution OODR photofragment spectroscopy provides direct experimental information about the long-range interaction and the predissociation mechanisms of molecular ions.

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