Vibrational Structure of the O_2^{2+} Ground State Observed by Threshold Photoelectron Coincidence Spectroscopy

R. I. Hall,[1] G. Dawber,[2] A. McConkey,[2] M. A. MacDonald,[3] and G. C. King[2]

[1]Laboratoire de Dynamique Moléculaire et Atomique, Université Pierre et Marie Curie,
4 place Jussieu T12-B75, 75252 Paris CEDEX 05, France

[2]Department of Physics, Schuster Laboratory, Manchester University, Manchester M13 9PL, United Kingdom

[3]Science and Engineering Research Council Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom

(Received 21 January 1992)

Double ionization of O_2 induced by photons from a synchrotron radiation source has been studied in an electron-electron coincidence experiment. A new technique has been developed wherein only electrons with near zero energy are detected by use of the penetrating field method. In this way high sensitivity and energy resolution have been attained allowing nineteen vibrational levels of the O_2^{2+} ground state to be observed and molecular parameters of this state to be obtained.

Doubly charged positive ions or dications of molecules have been known to exist since 1921 when Thomson [1] reported the observation of what was proposed to be either N_2^{2+} or CO^{2+}. Another ten years elapsed before Vaughan [2] reported the first determination of a double-ionization potential, namely, that of CO. Strictly speaking, these ions are not stable, as the Coulomb repulsion between the atomic ions leads to a system whose potential energy is everywhere greater than the dissociation energy. However, the binding force produced by the exchange interaction between the electrons can shield the Coulomb interaction and produce a local potential minimum, thus preventing dissociation by the formation of a barrier. The height of the potential barrier in many cases is such that the potential well can contain several vibrational levels whose lifetimes are so long that the ion can be considered stable.

Since their discovery, very little precise experimental information has been obtained on the electronic states of molecular dications. This situation does not result from a lack of effort as a whole variety of techniques have been applied to their study [3-12]. Despite this activity most of our knowledge of the structure of diatomic dications depends on theoretical calculations and this is particularly true for molecular oxygen.

Potential curves for the ground and first excited states of O_2^{2+} are shown in Fig. 1. These potentials were calculated by Pettersson and Larsson [13] and are in fact very similar to those recently presented by other authors [14-16]. The form of the ground-state potential curve is typical of molecules for which quasistable dications have been observed. The potential well is several eV deep and, according to Pettersson and Larsson [13], contains eighteen vibrational levels. The only available experimental information on the O_2^{2+} ground state was obtained indirectly in a fast-ion-beam experiment [17]. The double-ionization potential could not be determined in that experiment but a recent measurement located it at 36.6 ± 0.1 eV [4], and there are several other determinations available in the literature. In fact this fundamental

parameter of a simple molecule is represented by a series of low-precision values spread over a large energy range.

Here we report a new type of photoelectron spectroscopy using synchrotron radiation wherein double-ionization processes are detected by recording the coincidences between two essentially zero-energy electrons. We call this technique threshold photoelectron coincidence (TPES-CO) spectroscopy. The technique provides high energy resolution, sensitivity, and detection efficiency, allowing double-ionization processes to be probed within a few meV of their thresholds. In this way the vibrational structure of the $X\,^1\Sigma_g^+$ ground state of O_2^{2+} has been observed for the first time, thus allowing vibrational constants to be determined and an accurate value for the double-ionization energy of O_2 to be obtained.

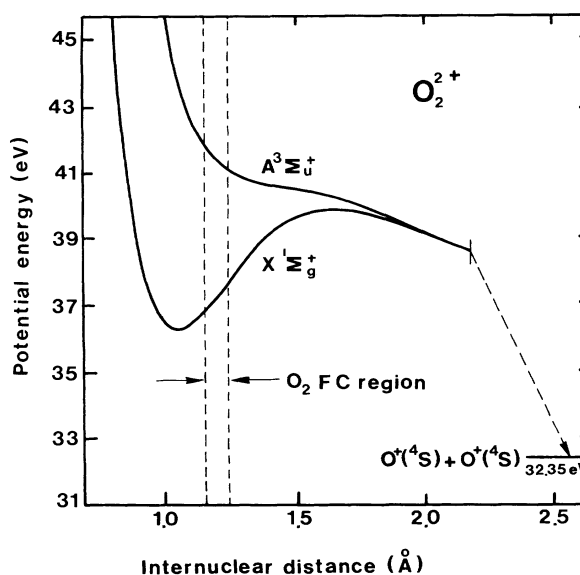The main elements of the apparatus are a photon

FIG. 1. Theoretical potential-energy curves of the ground and first excited states of O_2^{2+} calculated by Pettersson and Larsson [13].
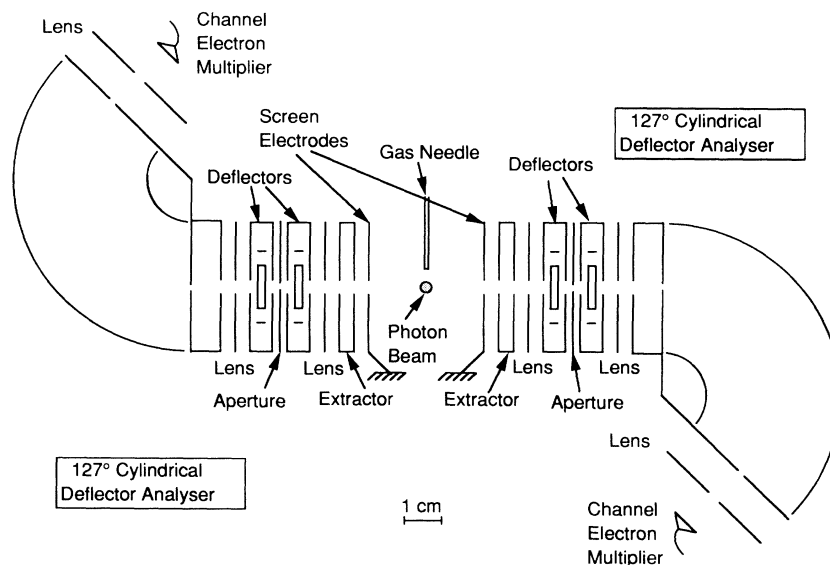
FIG. 2. Schematic diagram of the TPESCO spectrometer.

beam, an effusive gas beam, and two electron energy analyzers, and these are shown schematically in Fig. 2. The photon beam was provided by the Daresbury Laboratory Synchrotron Radiation Source via a toroidal grating monochromator. The photon beam enters the apparatus via a 1-mm-diam capillary where it intersects the gas emanating from a hypodermic needle. It is possible to adjust externally the position of the needle with respect to the scattering region and to change the potential applied to the needle. These provisions are found to be essential for near-threshold studies.

The coincidence spectrometer consists of a pair of 127° cylindrical deflector analyzers (CDA) placed on opposite sides of the interaction region. They were developed from the photoelectron analyzer described by King et al. [18] and are each tuned to collect zero-energy electrons using the penetrating field technique. This technique was first described by Cvejanović and Read [19] and more recently by Hall et al. [20] and provides a very large collection angle and furthermore forms a crossover point in the electron trajectories which ensures their efficient transmission through the subsequent optics. Electrons transmitted by the analyzers are detected using channel electron multipliers. Coincidences are measured between electrons detected by the two analyzers using standard timing electronics. This instrument is a development of and a considerable improvement on the one described previously [20].

The collection mode of the coincidence spectrometer was set up by balancing the potentials (and the needle potential) in such a way that at the threshold of a photoionization process the yield of zero-energy electrons was divided equally between the two analyzers. At the threshold, double ionization yields two zero-energy electrons which can drift towards different analyzers. A true coin-

cidence signal is then the signature of a double-ionization event and will be recorded each time the scanned photon energy goes through the threshold of a double-ion state. A TPESCO spectrum obtained in this way is then the double-ionization analog of threshold photoelectron spectra used in the study of single-ionization processes [21-23].

A TPESCO spectrum showing a long series of vibrational levels which are assigned to the O_2^{2+} ground state is presented in Fig. 3. The peak widths in this spectrum represent an overall instrumental resolution of 80 meV which corresponds to the energy spread of the photon beam. The coincidence count rate at the most intense peak was about 0.5 count/sec for less than 0.1 random coincidence count/sec. The energy scale was calibrated using an admixture of O_2 and argon against the Ar^{2+} $^3P_2$ threshold at 43.38 eV. The first peak in the spectrum is clearly the $v = 0$ level, and the double-ionization potential of O_2 represented by this level is located at 36.13 ± 0.02 eV.

Nineteen vibrational levels of the ground state can be observed in the spectrum and their energies were obtained by fitting a Gaussian function of fixed width to each of the vibrational peaks. The fitting procedure also revealed that levels above $v = 8$ are superimposed on a rising background. This background is depicted as a dashed line and will be discussed below. The peak energies thus obtained are shown in Fig. 3 by the vertical ticks.

The vibrational motion of the lowest levels of diatomic molecules is well represented by that of an anharmonic oscillator and the vibrational energies are given by the expression

$$E(v) = T_0 + \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2$$
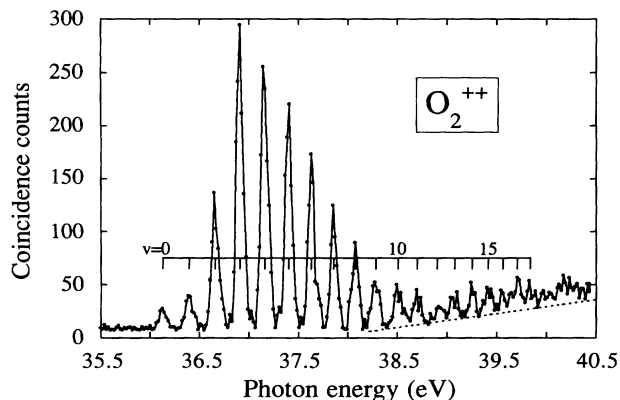$$+ \omega_e y_e(v + \tfrac{1}{2})^3 + \cdots ,$$

FIG. 3. TPESCO spectrum showing vibrational levels of the O_2^{2+} ground state.

FIG. 4. Normalized intensity distribution of the O_2^{2+} vibrational levels observed in the TPESCO spectrum compared to the normalized Franck-Condon factors between the O_2 ground level and the O_2^{2+} ground state calculated using the theoretical potential of Pettersson and Larsson [13].

where T_0 is the potential minimum referred to the $v = 0$ level of the ground state and ω_e, $\omega_e x_e$, $\omega_e y_e$ are the vibrational constants. A fit of this expression to the observed energies of the first eight levels gave the following values for the molecular constants: $T_0 = 35.991 \pm 0.002$ eV, $\omega_e = 0.276 \pm 0.001$ eV, and $\omega_e x_e = 3.5 \pm 0.2$ meV, where the errors represent the statistical uncertainty. (However, and in order to avoid a long table, the energies of all nineteen observed levels are represented to within ± 0.01 eV by the following set of constants: $T_0 = 36.00$ eV, $\omega_e = 0.267$ eV, $\omega_e x_e = 2.1$ meV, and $\omega_e y_e = -5.8 \times 10^{-5}$ eV).

The more recent theoretical values for ω_e and $\omega_e x_e$ compare quite favorably with those observed in the present work. Pettersson and Larsson [13] gave $\omega_e = 0.266$ eV, $\omega_e x_e = 2.9$ meV whereas Wong et al. [14] found 0.278 eV and 2.9 meV for these constants, respectively. However, the agreement with T_0 is less satisfactory, the former obtaining 36.27 and the latter 35.66 eV.

Single-photon double ionization can proceed by either one-step or two-step mechanisms. In the one-step mechanism two electrons are ejected into the continuum and the process is governed by electron correlations. The two-step process takes place by the formation of a singly charged ion in an excited state that subsequently autoionizes to form a lower state of the dication. Autoionization has revealed itself to be particularly efficient in the double ionization of the heavier rare gases [24] and this would also appear to be the case for molecules as has been demonstrated recently by Price and Eland [9]. The presence of indirect processes would hamper identification of the structure in the TPESCO spectrum as they would tend to distort the intensity envelopes of the vibrational series. This mechanism would also be expected to lead to the observation of levels outside the Franck-Condon region. This is the situation for the analogous single-ionization threshold photoelectron spectrum of O_2 where autoionizing neutral states produce erratic peak envelopes and lead to the detection of high levels well
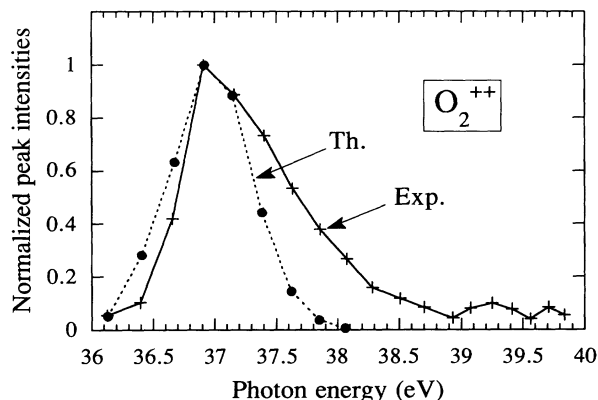
outside the Franck-Condon region [22].

The experimental vibration peak intensities are shown in Fig. 4. Also shown are the Franck-Condon factors between the $v = 0$ level of the neutral ground state and the vibrational levels of the dication which we obtained using the potential curve given by Pettersson and Larsson [13]. The energies of these latter levels have been shifted downwards by 0.27 eV so that the energy of the $v = 0$ level coincides with that observed and the intensities are normalized to unity at the most intense peak. The general agreement between the two envelopes is reasonable. If we suppose that double ionization is a one-step process and governed by a single set of Franck-Condon factors, and the smooth intensity envelope would argue in favor of this, then the observed intensities would indicate that the internuclear separation of the theoretical potential curve should be reduced slightly. On the other hand, the fact that very high levels are observed with appreciable intensity does suggest the presence of indirect processes. No translation of the theoretical potential curve could account for the observed intensities in the high levels while correctly describing the envelope of the lowest levels. Note that the $O_2^+ (2s\sigma_g^{-1})$ state has been identified in this energy region in x-ray photoionization experiments [10].

Information about the origin of the underlying background in Fig. 3 can be obtained from the observations of Price and Eland [9] obtained in a photoionization experiment using light from a helium lamp. In this study, intermediate states were found to autoionize to the repulsive part of the potential curve of the dication outside the potential barrier at separations such that they corresponded to atomic autoionizing transitions identifiable by the well-defined energies of the ejected electrons [25]. On being excited at the threshold these intermediate states would yield a zero-energy electron and could then

produce a second one either as the potential curves cross into the double ion continuum or as an atomic transition following complete nuclear separation. This mechanism would explain the background with an onset at 38.2 eV lying underneath the high vibrational levels.

In summary, a vibrational series of the ground state of a molecular dication, that of oxygen, has been observed for the first time in a photoionization experiment. At least nineteen levels of this series have been identified and this has allowed the molecular constants to be deduced. The double-ionization potential of O_2 has been located at 36.13 ± 0.02 eV. This value is nearly 0.5 eV lower than the currently accepted value, a difference explainable by the relatively low intensity of the first two vibrational levels. These results are in good agreement with the results of modern theoretical calculations using configuration interaction techniques and large computers and this demonstrates the high quality of these calculations, particularly regarding molecular parameters. At the present time, theory still represents our main source of knowledge concerning the structure of molecular dications but the technique described herein should in the future greatly increase the quality of experimental data, especially as we are at present limited by the resolution and flux of the photon source. As the next generation of synchrotrons becomes available, this limit should be lifted.

[1] J. J. Thomson, *Rays of Positive Electricity* (1921), p. 84, reference taken from Vaughan [2].

[2] A. L. Vaughan, Phys. Rev. **38**, 1687 (1931).

[3] F. H. Dorman and J. S. Morrison, J. Chem. Phys. **35**, 575 (1961).

[4] M. Hamdan and A. G. Brenton, Chem. Phys. Lett. **164**, 413 (1989).

[5] P. Lablanquie *et al.*, Phys. Rev. A **40**, 5673 (1989).

[6] G. Dujardin, L. Hellner, M. Hamdan, A. G. Brenton, B. J. Olsson, and M. J. Besnard-Ramage, J. Phys. B **23**, 1165 (1990).

[7] J. H. D. Eland, S. D. Price, J. C. Cheney, P. Lablanquie, I. Nenner, and P. G. Fournier, Philos. Trans. R. Soc. London A **324**, 247 (1988).

[8] L. Hellner, M. J. Besnard, and G. Dujardin, Chem. Phys. **119**, 391 (1988).

[9] S. D. Price and J. H. D. Eland, J. Phys. B **24**, 4379 (1991).

[10] K. Siegbahn *et al.*, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1965).

[11] P. C. Cosby, R. Möller, and H. Helm, Phys. Rev. A **28**, 766 (1983); D. M. Szaflarski, A. S. Mullin, K. Yokoyama, M. N. R. Ashfold, and W. C. Linerberger, J. Phys. Chem. **95**, 2122 (1991).

[12] D. Cossart, F. Launay, J. M. Robbe, and G. J. Gandara, Mol. Spectrosc. **113**, 142 (1985).

[13] L. G. M. Pettersson and M. Larsson, J. Chem. Phys. **94**, 818 (1991).

[14] M. W. Wong, R. H. Nobes, W. J. Bouma, and L. Radom, J. Chem. Phys. **91**, 2971 (1989).

[15] B. X. Yang, D. M. Hanson, and K. Tohji, J. Chem. Phys. **89**, 1215 (1988).

[16] M. Larsson *et al.*, J. Phys. B **23**, 1175 (1990).

[17] W. J. van der Zande, Chem. Phys. **157**, 287 (1991).

[18] G. C. King, M. Zubek, P. M. Rutter, and F. H. Read, J. Phys. E **20**, 440 (1987).

[19] S. Cvejanović and F. H. Read, J. Phys. B **7**, 1180 (1974).

[20] R. I. Hall, A. McConkey, K. Ellis, G. Dawber, L. Avaldi, and G. C. King, Meas. Sci. Tech. **3**, 316 (1992).

[21] D. Villarejo, J. Chem. Phys. **48**, 4014 (1968).

[22] M. Richard-Viard, O. Dutuit, M. Lavollée, T. Govers, P. M. Guyon, and J. Durup, J. Chem. Phys. **82**, 4054 (1985).

[23] M. Sander, L. A. Chewter, K. Müller-Dethlefs, and E. W. Schlag, Phys. Rev. A **36**, 4543 (1987).

[24] R. I. Hall, K. Ellis, A. McConkey, L. Avaldi, M. A. MacDonald, and G. C. King, J. Phys. B **25**, 377 (1992).

[25] A. A. Wills, A. A. Cafolla, and J. Comer, J. Phys. B **24**, 3989 (1991).

Lens

Channel
Electron
Multiplier

Screen
Electrodes

Gas Needle

Deflectors

127° Cylindrical
Deflector Analyser

Deflectors

Photon
Beam

Lens

Aperture

Lens

Extractor

Extractor

Lens

Aperture

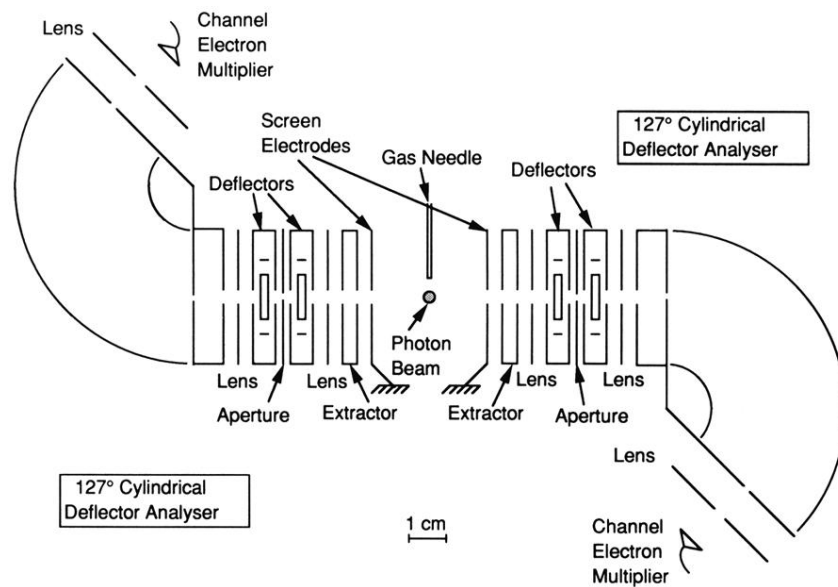Lens

127° Cylindrical
Deflector Analyser

1 cm

Lens

Channel
Electron
Multiplier

FIG. 2. Schematic diagram of the TPESCO spectrometer.