Novel Time of Flight Instrument for Doppler Free Kinetic Energy Release Spectroscopy

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(Received 14 November 1994)

A novel Doppler free coincidence time-of-flight technique is presented. The technique allows kinetic energy release spectra to be obtained at vibrational resolution. The only limitation of the technique from a resolution point of view is the thermal rotational distribution in the neutral ground state, 25 meV FWHM at 300 K, which is directly reflected in the line profiles. As a test case the CO^{2+} ion is studies. Well resolved vibrational progressions are observed for the first time in a coincidence kinetic energy release spectrum.

PACS numbers: 34.50.Lf

Doubly charged diatomic molecules have been studied extensively. An overview of some experimental and theoretical techniques concerning multiply charged molecules has been given in [1].

This Letter presents a new coincidence time-of-flight (TOF) instrument. Earlier techniques for ion kinetic release measurements are ion translational energy spectroscopy (TES) including double charge transfer spectroscopy (DCT) [2–5], photoion-photoion coincidence spectroscopy (PIPICO) [2], and ion kinetic energy release spectroscopy (IKES) [6–10]. Threshold photoelectrons coincidence spectroscopy (TPESCO) [11] has recently given detailed information of the energy levels in doubly charged molecules, but in contrast to the present method it gives no information about the dissociation channels. A prestudy of the present method can be found in [12].

Ion fragment measurements in coincidence in principle give the kinetic energy release, but earlier results, obtained using *only one channel* for energy analysis and the pulses from the other detector simply as a coincidence requirement [9,10], have suffered from poor resolution due to Doppler broadening in the kinetic energy distribution of the fragments. For a randomly moving diatomic molecule AB at temperature T, dissociating into two fragments of masses m_A and m_B yielding a total kinetic energy release E, the FWHM of the resulting Doppler broadened line in either fragment is given by

$$\frac{4}{m_A + m_B}\sqrt{\ln 2 m_A m_B E k T}\,, \qquad (1)$$

assuming that the fragment energies are much higher than the thermal energy.

For example, a stationary CO molecule dissociating with 8.00 eV total energy release produces two ions with 4.57 and 3.43 eV kinetic energy, respectively. The FWHM Doppler broadening at 293 K resulting from individual measurements of either of these fragment energies is 0.74 eV.

By measuring both fragment energies, E_A and E_B, we can eliminate the center of mass kinetic energy. The dissociation energy is then given by

$$E = E_A + E_B - \frac{[\sqrt{E_A m_A} - \sqrt{E_B m_B}]^2}{m_A + m_B}. \qquad (2)$$

This calculation has to be performed in real time for each coincident pair.

Our instrument will be described in detail elsewhere [13]. Briefly, the target gas is ionized in a differentially pumped gas cell by a pulsed electron beam of a few μA. The pulse length is adjustable between 5 and 1000 ns and typical repetition rates are 2–10 kHz. Two 50 cm long field free TOF tubes are mounted in a 180° geometry with a gridded 40 mm microchannel plate (MCP) detector at each end. All surfaces facing low energy ions are coated with graphite. The resulting detector pulses are processed in a data acquisition unit based on a microprocessor controlled 100 MHz timer. The width and position on the time-of-flight axis of the coincidence window varies continuously with the time after ionization, in order to roughly correspond to the expected thermal distribution. If two pulses occur within a pair of windows that corresponds to the average relative flight times for the two fragments, they are interpreted as a coincident pair, and their respective times of flight are transferred to a personal computer. The true release energy is calculated according to Eq. (2), with due consideration to the fact that the energy channel width is dependent on the flight times for the fragment pair plotted. In a typical case, the count rate at each detector is about 1000 counts/s (cps), whereas the typical rate of coincidences processed by the personal computer is 1 cps. The upper count rate limit is solely determined by the occurrence of random coincidences. A schematic picture of the experimental setup is shown in Fig. 1.

Because of the particle flux in the gas cell, the surface potential in the cell may differ by ±0.5 V from other surfaces. Consequently, the zero of the energy scale is uncertain within ±1 eV. A preliminary calibration was performed using deuterium since the peak of the kinetic energy distribution from dissociating ${D_2}^{2+}$ can be calculated accurately within ±50 meV. A reflection approximation calculation [14] gives a peak position of 18.80 eV. Deuterium was mixed with the gas under investigation, and the resulting composite spectrum was easily analyzed due to the short time of flight of the deuterons. This calibration is sufficiently accurate to allow identification of vibrational states.

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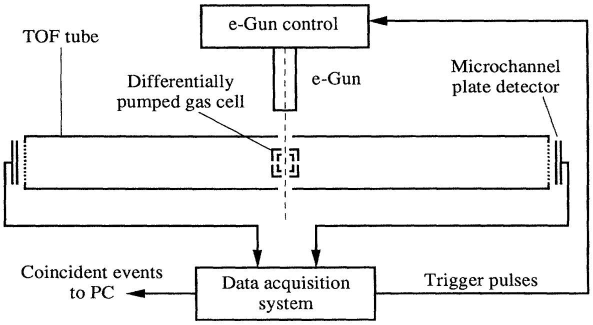

FIG. 1. Schematic picture of the experimental setup.

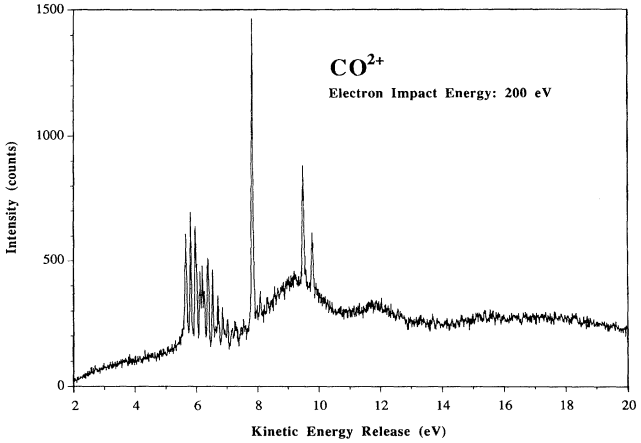

FIG. 2. Doppler free energy release spectrum of CO^{2+}.

In the data acquisition program each TOF tube is modeled as consisting of two potential regions, the gas cell and the remaining parts of the tubes. This potential model is used for the conversion between measured times of flight and the total kinetic energy release.

As in all measurements of the kinetic energy of charged particles emitted from gases, the work function of the gas cell may change slowly during the data acquisition. This means that the energy scale will show a corresponding drift. Neglecting this will lead to impaired resolution. In our device, this drift is compensated by a stabilization method developed earlier for high resolution photoelectron spectroscopy [15]. The method uses successive particle spectra obtained in parallel to the recording of the total energy release spectrum. The correlation function between each partial spectrum and the very first one obtained is calculated. Any shift in the correlation function maximum is then interpreted as caused by a change in the work function of the gas cell. The potential model of the spectrometer is modified accordingly, thus changing the time-to-energy conversion function. Hence, any drift is compensated for in software at regular intervals during the whole measurement.

In order to investigate the factors that influence the instrumental resolution we used a Monte Carlo simulation. In this simulation the thermal velocity of the neutral molecule was assumed to follow the Maxwell-Boltzmann distribution. At zero pulse length the FWHM of the simulated peaks was found to be close to 1:1000 of the kinetic energy release, which is the theoretical limit of the instrumental resolution in the present geometry. In our CO test case, where we used a pulse length of 100 ns, the simulated widths at 6 and 10 eV were found to be 13 and 29 meV, respectively. In addition to the instrument dependent broadening, the peaks also should have a natural broadening of about 25 meV due to the thermal population of the rotational levels.

If the lifetime of a vibrational state is long enough, the instrument will produce an asymmetric line profile with a decay slope to the low energy side, since the delay will be interpreted as a longer time of flight and thus a lower kinetic energy.

The data acquisition software assumes for simplicity that the lighter fragment always is allotted one specific detector. For a molecule with a large atomic mass ratio, where the heavier fragment always will be detected after the lighter one, half of the detected fragments will thus be sorted out as nocoincident events. For nearly isobaric molecules, such as CO, any fragment may achieve the shortest time of flight due to the center of mass motion. In other words, their coincidence windows overlap each other. The fragments of "wrong" identity cannot be sorted out, but fortunately this is not necessary as the Doppler reduction algorithm is symmetric in the fragment

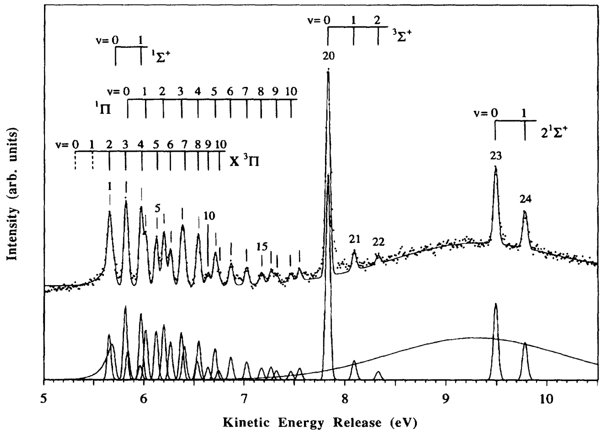

FIG. 3. Doppler free energy release spectrum of CO^{2+} between 5 and 10.5 eV. The experimental result is indicated by dots, and Gaussian distributions fitted to the experimental data are shown below. Their total sum is added to the background and indicated by the solid line. The vibrational progressions to the corresponding electronic states are represented by the bar diagrams.

masses. These coincidences, originating from a very rapidly moving center of mass, will then nevertheless yield the correct energy release.

If a molecule is located off center in the gas cell when ionized, the corresponding shift in the flight time of the two fragments will also be interpreted as a Doppler shift by the coincidence algorithm. The calculated correction to the release energy is sufficiently close to the correct value to make the width of the exciting beam of much less importance here than in other time-of-flight experiments.

As a test case, we have acquired a spectrum of CO^{2+} between 2 and 20 eV at 200 eV impact energy, which is shown in Fig. 2. In principle, the spectrum contains information about CO^{q+}, where $q \geq 2$. We assume, however, first that the more highly charged ions probably have an order of magnitude smaller probability of being formed, and secondly that they most likely do not have quasibound states. Hence, we assign all sharp structures to reflect dissociation from CO^{2+}. The pressures in the gas cell and the TOF tubes were about 2×10^{-4} and 1×10^{-6} Torr, respectively, and the recording time was 226 h. Figure 3 shows a detail of the spectrum where we have assigned five vibrational progressions belonging to the $X\,^3\Pi$, $^1\Sigma^+$, $^1\Pi$, $^3\Sigma^+$, and the $2\,^1\Sigma^+$ electronic states, as show in the figure. Two broad structures at 9.3 and 11.8 eV with FWHM's of about 2 eV are discerned in the same region. Experimental data for 24 peaks are collected in Table I. Note that some of the numbered peaks contain more than one component. The energies refer to Gaussian functions fitted to the peaks, and the given intensities represent the relative areas of the Gaussians above the broad structures and the background.

TABLE I. Experimental release energies of the vibrational levels in different electronic states in CO^{2+} together with the corresponding vertical energies and intensities. Some of the numbered peaks have contributions from more than one state.

State	Vib. Lev.	Release energy (eV)	Composite peak No.	Relative intensity	Vertical energy (eV)[a]	Vertical energy (eV)[b]
$X\,^3\Pi$	0					41.294
	1					41.474
	2	5.655	1	19	41.632	41.626
	3	5.816	2	31	41.793	
	4	5.973	3	28	41.950	
	5	6.124	5	21	42.101	
	6	6.266	7	16	42.243	
	7	6.404	8	15	42.381	
	8	6.530	9	8	42.507	
	9	6.638	10	6	42.615	
	(10	6.745	12	4	42.722)	
$^1\Sigma^+$	0	5.713	1	43	41.690	41.700
	(1	5.963	3	6	41.940	41.938)
$^1\Pi$	0	5.841	2	12	41.818	41.814
	1	6.021	4	21	41.998	42.004
	2	6.199	6	24	42.176	42.187
	3	6.375	8	20	42.352	42.364
	4	6.547	9	17	42.524	42.534
	5	6.710	11	14	42.687	42.697
	6	6.870	13	10	42.847	42.853
	7	7.027	14	8	43.004	43.002
	8	7.174	15	5	43.151	43.145
	9	7.321	17	4	43.298	43.281
	10	7.465	18	4	43.442	43.410
$^3\Sigma^+$	0	7.833	20	100	43.810	43.573
	1	8.093	21	9	44.070	43.826
	2	8.333	22	4	44.310	44.073
$2\,^1\Sigma^+$	0	9.493	23	40	45.470	45.470[c]
	1	9.785	24	20	45.762	45.785
...		7.268	16	6	43.245	
...		7.553	19	6	43.530	

[a] This work.

[b] Reference [11].

[c] Corrected value according to Reference [15].

The FWHM is typically 50 meV, which corresponds to the Doppler broadening in CO cooled to less than *3 K*. The error in the relative peak positions is believed to be less than 10 meV, and the absolute energy scale is referred to the position of peak 23 as obtained from the TPESCO spectrum of CO^{2+} in Ref. [11], slightly corrected [16]. Assuming dissociation to the ground ionic states, this peak should appear at 9.493 eV in our spectrum since the fragments are left at 35.977 eV above the neutral ground vibrational state of CO according to handbook data [17,18].

Apart from a somewhat better resolution than in Ref. [11], the new information obtained on CO^{2+} from this experiment is the following:

(1) All observable discrete states of the dication dissociate into the ground ionic states $C^+(^2P) + O^+(^4S)$ by coupling to a repulsive $^3\Sigma^-$ state. Tunneling through the potential barrier should only be responsible for a minor contribution to the dissociation except for the $2\,^1\Sigma^+$ state where tunneling lifetimes are of the same order of magnitude as the electronic predissociation rates [19,20].

(2) The $v = 0$ and $v = 1$ levels of the $X\,^3\Pi$ state are not visible due to their long lifetime, as partly supported by [20]. The absence of these levels in our recording indicates that their lifetime is well above 3 μs.

(3) Peak 1 is composed of the Gaussian $v = 2$ level of the $X\,^3\Pi$ and the $v = 0$ level of the $^1\Sigma^+$ states, which is asymmetrically broadened towards the low energy side, corresponding to a lifetime of 600 ± 100 ns.

(4) All the other observed vibrational levels must have lifetimes in the interval 1×10^{-14}–5×10^{-8} s. Otherwise the lines would have been visibly broadened and, in the case of longer lifetimes, asymmetrically shaped.

Using our experimental release energies, the corresponding vertical energies are calculated. The results are included in Table I together with the experimental results of Ref. [11]. The agreement is good except with respect to the assignment of peak 20, which we assume to be the $v = 0$ level. According to Ref. [21] , the authors of Ref. [11] also proposed this identification as an alternative.

In conclusion, we have shown that by eliminating the Doppler broadening in the kinetic energy distribution of ion fragments the resolution of energy release spectra can be improved so much as to resolve the vibrational structure in quasibound electronic states. A detailed discussion of the spectrum shown here, and also of similar spectra of O_2 and N_2 will be published separately [22].

Mats Larsson at the Royal Institute of Technology in Stockholm is acknowledged for submitting theoretical data on potential curves. Lars Bolkegård and Jan-Olof Forssell are acknowledged for the physical realization of the apparatus, and Karl-Göran Görsten at Gammadata Mätteknik AB for the development of the software in the coincidence analyzer. This work was supported by the Swedish Natural Science Research Council.

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