RESEARCH ARTICLE

Do the O₂ Schumann–Runge Bands Participate in keV Collision-Induced Dissociation Experiments?

Yawei Lin, Paul M. Mayer

Department of Chemistry, University of Ottawa, 10 Marie-Curie, Ottawa, ON, Canada K1N 6N5

Abstract

In high-energy (keV) CID experiments, oxygen has the unique ability to enhance specific ion fragmentation pathways that lie within a relatively narrow band of activation energy. It has been previously proposed that this oxygen-enhanced dissociation phenomenon is due to the participation of the O₂ B³Σ_u⁺ – X³Σ_g[–] (Schumann–Runge) system in the collision complex. During the collision, oxygen is first excited to its B³Σ_u⁺ state before it returns this energy to the projectile ion. This energy drives the nonstatistical dissociation of the projectile provided there is an energetically accessible pathway in resonance with the absorbed radiation. To probe the validity of this hypothesis, a modified VG-ZAB mass spectrometer was used to observe the photon emissions from keV collisions of a selection of projectile ions with O₂ target gas. By studying the resulting collision-induced emission (CIE) spectra, a second potential mechanism came to light, one that involves the near-isoelectronic O₂⁺ A²Π_u → X²Π_g state transition.

Key words: Collision-induced dissociation, Collision-induced emission, Oxygen target gas, Charge transfer excitation, Schumann–Runge band system, Oxygen ion emission band system

Introduction

In mass spectrometry, ion dissociation may occur either spontaneously (metastable ion) or due to (intentionally supplied) additional activation. Such activation is typically achieved through collisions with neutral target gases, a process called collision-induced dissociation (CID). In a magnetic sector mass spectrometer, CID mass spectra are obtained by colliding mass-selected ions that have keV lab frame energies with a stationary target gas. During the keV ion–target collision, part of the translational energy of the projectile ion can be converted into internal energy, and this internal energy is assumed to be redistributed statistically

among the internal degrees of freedom, in the form of vibrational energy in the ground state, prior to dissociation [1, 2]. In this assumption, the CID mass spectra resulting from the various competing dissociation pathways are independent of how the ion obtained its internal energy in the first step.

Various target gases can be used to obtain CID mass spectra, such as N₂, Ar and He. According to empirical observations, the CID mass spectra attained using different target gases are quite similar [3]. However, O₂ behaves differently from most target gases in that it can significantly favor some specific fragmentation reactions. This non-ergodic behavior of O₂ has aroused the interest of several groups. Flammang et al. reported a series of O₂-enhanced dissociations in CID mass spectra and compared them with those of other common target gases, such as N₂ and Ar [4–8]. Holmes et al. [9, 10] performed a systematic study of O₂-enhanced dissociations, including the loss of CH₃ from CH₃CH⁺X (X = OH, NH₂, SH, CH₃), the loss of CH₃ and

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Correspondence to: Paul M. Mayer; e-mail: pmmayer@uottawa.ca

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Cl. from CH₃C⁺(Cl)CH, the loss of C₂H₅. from CH₃CH₂CH⁺X (X = OH and NH₂), the loss of H. from ⁺CH₂OH and ⁺CH₂NH₂, and the loss of O from 1,2-, 1,3- and 1,4-C₆H₄(NO₂)₂⁺, etc. They found that these dissociation reactions share some common features in that they are all high-energy simple bond cleavage reactions. Moreover, their minimum energy requirements all fall within a relatively narrow energy range (450–565 kJ mol⁻¹). Some examples are shown in Figure 1. In the ⁺CH₂OH CID mass spectrum, the peak with *m/z* 30 (fragment ion from the loss of H. from ⁺CH₂OH) is more intense when O₂ is used as the target gas rather than He, indicating that H. loss from ⁺CH₂OH is an O₂-enhanced dissociation. The ⁺CH₂NH₂ CID mass spectrum shows the same pattern. The reaction leading to O loss from the nitromethane cation, CH₃NO₂⁺ (which produces a peak with *m/z* 45), does not thermochemically fall within the above energy window (229 kJ/mol), but enhancement is still observed. Note that the fragment ion peak exhibits significant broadening due to the release of kinetic energy during the dissociation, an indication that this channel involves a large reverse-energy barrier. The authors speculated that though the reaction energy, Δ*H*, is 229 kJ mol⁻¹, the real energy requirement for this fragmentation could still fall within the 450–565 kJ mol⁻¹ energy range [10]. To rationalize these observations, the specific energy range of the dissociation was correlated to a property of the O₂ target itself. It has been reported [16] that the B³Σ_u⁺ state of O₂ has a long lifetime (in the range of milliseconds), and also that its potential energy relative to the X³Σ_g⁻ ground state is 598–682 kJ/mol (the latter being the dissociation limit of O₂ to O(³P) to O(¹D), as shown in Figure 2), which is close to the O₂-enhancement dissociation energy window. Accordingly, it was proposed [10] that O₂ was excited from the ground X³Σ_g⁻ state to the B³Σ_u⁺ state (belonging to the B³Σ_u⁺ – X³Σ_g⁻ Schumann–Runge system), and that this B state of O₂ resonantly transfers this

energy quantum back to the projectile ion in the collision complex, allowing the ion to undergo dissociations with activation energies that lie within that range.

Although the hypothesis explained the experimental results very well, there has been no concrete experimental evidence for the formation of the O₂ B state during the collision. It is known that when excited states of a species are produced during the collision process, some of them will transit to lower states, emitting characteristic photons with specific wavelengths when they do so (collision-induced emission, CIE). In this study, CIE spectra were obtained for different ion–O₂ collisions in order to probe the excited electronic states produced, especially the O₂B³Σ_u⁺ → X³Σ_g⁻ SR emission band (the only observed emission associated with the B³Σ_u⁺ state [16]).

Experimental Procedures

All experiments were performed on a modified VG ZAB mass spectrometer. The original, double-focusing mass spectrometer [11–13] was employed with an added third field-free region (3FFR), as previously described [14, 15]. Ions were generated with 80–90 eV electron ionization in the ion source of the instrument. The ions were transmitted to the 3FFR, where they collided with the target gas in the collision cell at a collision gas pressure that reduced the pre-cell ion flux by 10% or 40% as needed.

A spectrograph (Acton SpectraPro 275, 27.5 cm focal length, 1200 g mm⁻¹ holographic grating; Acton Research Corp, Acton, MA, USA) and a thermoelectrically cooled charge-coupled device (CCD) detector (Andor DV401-UV, front-illuminated with UV coating; Andor Technology, Belfast, UK) were installed above the collision cell to detect photons emitted due to ion–target collisions [15]. Emissions from the excited state species were observed directly with the CCD detector cooled to a temperature of -35 °C. The

Figure 1. Partial He and O₂ CID mass spectra of (a) source ⁺CH₂OH, (b) source ⁺CH₂NH₂, and (c) CH₃NO₂⁺, from Holmes et al. [10]. Republished with permission from Aubry, C., Holmes, J.L.: The behavior of oxygen as a collision-induced dissociation target gas. *J Am. Soc. Mass Spectrom.* **12**(1), 23–29 (2000)

Figure 2. Potential energy diagram of O₂ and O₂⁺ from Krupenie [16]. Republished with permission from Krupenie, P.H.: Spectrum of molecular oxygen. *J. Phys. Chem. Ref. Data.* 1(2), 423–534 (1972)

entrance slit of the spectrograph was set to 3.0 mm, providing a spectral resolution of 8.5 nm (measured at full width at half-height for atomic lines). Optical emissions were recorded from 190 to 1020 nm using the Andor MCD 2.63.1.8 program and recorded in 14 separate segments, each of which was 50–70 nm wide. The data were accumulated in two periods, ranging from 1 h to 4 h, at an ion translational energy of 8 keV for each segment in full vertical binning reading mode. Each segment had the background subtracted, and background spectra were collected prior to signal acquisition under exactly the same conditions except without an ion beam. Spectral spikes resulting from cosmic rays were removed digitally by the program. Horizontal binning was performed manually in the ASCII file by combining the data from every 20 pixel columns, and the overlapping portion of the spectrum at the two ends of each window was averaged.

Higher-resolution spectra were obtained by reducing the entrance slit width to 1.0 or 0.5 mm, resulting in a spectral resolution of 3.0 or 2.4 nm, and the data acquisition time of each segment was increased to 8 or 10 h. Throughout the accumulation period, the ion flux intensity was monitored

and adjusted to ensure that it remained stable, and each segment was normalized to the flux intensity of the ion beam.

Results and Discussion

The Schumann–Runge (SR) system ($B^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$) is the most extensively studied system of O₂; more than a hundred lines of this system have been identified. The emission bands range from 207 to 535 nm, are red-degraded, and show no prominent band heads. Most other O₂ transitions are considerably weaker than the $B^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ system, as they are forbidden by electric dipole selection rules.

The CH₃NO₂⁺ target system was studied as CH₃NO₂⁺ ions can undergo O₂-enhanced dissociation, as mentioned in the “Introduction.” In the experiment, CH₃NO₂⁺ ion beams were prepared and sufficient target gas was supplied to achieve a 10% reduction in the beam (i.e., essentially single-collision conditions [11]). The resulting CIE spectra were obtained after two hours of accumulating signals for each section. Figure 3a shows the CIE spectra obtained from

Figure 3. (a) CIE spectra of CH₃NO₂⁺/O₂ and CH₃NO₂⁺/He: 10% beam reduction, slit width 3 mm; accumulation time 1 h. (b) CIE spectra of CH₃NO₂⁺/O₂ and CH₃NO₂⁺/He: 40% beam reduction, slit width 3 mm; accumulation time 2 h

CH₃NO₂⁺/O₂ and CH₃NO₂⁺/He in the range 190–570 nm, respectively. The CH₃NO₂⁺/O₂ CIE spectra exhibit three narrow atomic emission peaks of C (3s ¹P⁰→1p ¹D), H_β ($n=4 \rightarrow n=2$) and H_γ ($n=5 \rightarrow n=2$) [17], as well as a broad emission band ranging from 190 to 310 nm (i.e., well within the range of the SR band). In contrast, the CIE spectrum of CH₃NO₂⁺/He collisions exhibits no obvious emissions in this spectral range. Although the CIE spectrum of CH₃NO₂⁺/O₂ indicates that large amounts of excited C and H_β were produced during the collision, the ion fragment at m/z 49 (corresponding to the loss of C) is not shown in the O₂ CID mass spectrum. The m/z 60 (loss of H_β) peak has a similar intensity in the He and O₂ CID mass spectra. In 1987, McLafferty et al. [18] reported that the efficiency of the CID process was related to the ionization potential of the target gas, and Cooks' group [19] showed that the CID efficiency is greater for He targets because losses due to scattering and neutralization are reduced. Accordingly, the significant amounts of excited C and H_β that are only seen in the CIE spectrum of CH₃NO₂⁺/O₂ could be produced by dissociative charge transfer rather than CID.

In order to enhance the signal-to-noise ratio, target gas pressures were increased to produce a 40% reduction in the beam. The resulting CIE spectra are shown in Figure 3b. In the CIE spectrum of CH₃NO₂⁺/O₂, the peak at 314 nm was assigned to atomic emission from O⁺ (4s ⁴P⁰→3p ⁴D⁰) [17], again confirming that charge transfer reactions occur during ion–O₂ collisions. Although the strength of the broad peak increased, it was still too weak to be identified. The CIE

spectrum of CH₃NO₂⁺/He shows no obvious emissions, indicating that the unidentified broad peak could come from the target O₂.

The simpler N₂⁺/target gas system was also studied. Figure 4 shows the CIE spectra obtained from N₂⁺/O₂ and N₂⁺/He collisions in the range 190–570 nm. Both spectra show molecular emission from N₂⁺ and N₂ [20–22]. The broad feature in this region is now more intense, but again appears only in the N₂⁺/O₂ CIE spectrum, while N₂⁺/He collisions give only atomic emission from helium. Figure 5a shows a higher-resolution CIE spectrum for which the slits were narrowed from 3 to 1 mm and the accumulation time was increased from 2 to 8 h. The unknown broad peak showed obvious vibrational structure which enabled it to be identified. The best match to the experimental data was not found to be the O₂ SR bands, but rather A ²Π_u→X ²Π_g O₂⁺ ion emission, which falls in the same energy window (Figure 2). The O₂⁺ A→X emissions have obvious band heads and they are red-degraded and double-headed. The wavelengths of the A→X bands range from 194 to 653 nm, overlapping heavily with the SR band and thus making emission identification difficult. The vertical lines in Figure 5a show the O₂⁺ A→X emission bands reported in the literature [16], and agreement with the experimental data is excellent. However, the characteristic double heads of the bands were not observed, due to low resolution. Figure 5b shows the CIE spectrum with the slit width reduced to 0.5 mm. The spectrum shows that though the peak intensity weakens, we now observe the characteristic splitting of the A→X O₂⁺ emission bands, confirming the existence of a significant amount of O₂⁺ from charge transfer reactions. A full list of experimentally observed band heads and the reported O₂⁺ A→X emission bands is available in the [Electronic Supplementary Material](#).

Based on the above observation of the O₂ excited states produced, it is proposed that there are two possibilities: one is that there is no SR band formed in the collision; the other is that the A→X O₂⁺ emission produced from the charge transfer reaction between N₂⁺ and O₂ is so intense that it masks the SR

Figure 4. CIE spectra of N₂⁺/O₂ and N₂⁺/He: 40% beam reduction, slit width 3 mm, accumulation time 2 h. The bands that appear above 290 nm (marked by a circle) were identified as the emissions from N₂⁺ and N₂

Figure 5. (a) CIE spectrum of N₂⁺/O₂: 40% beam reduction, accumulation time 8 h, slit width 1 mm. (b) CIE spectrum of N₂⁺/O₂: 40% beam reduction, accumulation time 8 h, slit width 0.5 mm. Superimposed on the spectrum are the A²Π_u → X²Π_g O₂⁺ emission bands reported in the literature [15]

emission. To exclude the latter case, CH₃⁺ was chosen as a projectile ion (ionization energy = 9.84 eV; compare to 12.07 eV for O₂) [23], so that the charge transfer reaction producing the O₂⁺ ion is not thermochemically favored (a full table of all IE values for the compounds studied herein can be found in the [Electronic Supplementary Material](#)). Figure 6 shows the CIE spectra for CH₃⁺/O₂ collisions and the N₂⁺/O₂ system. Of course, the N₂⁺ and N₂ emissions were not observed, and two atomic emissions from C (3s ¹P⁰ → 1p ¹D) and O⁺ (4d ⁴P → 3p ⁴S⁰) were found. Band emission is also present and, compared with that from the N₂⁺/O₂ system, it is less intense and shows no well-resolved band heads. The accumulation time was increased from 8 to 10 h, and the resulting spectrum is shown in Figure 6b. The vertical lines

Figure 6. (a) CIE spectra of N₂⁺/O₂ and CH₃⁺/O₂: 40% beam reduction, accumulation time 8 h, slit width 1 mm. (b) CIE spectrum of CH₃⁺/O₂: 40% beam reduction, accumulation time 10 h, slit width 0.5 mm. Superimposed on the spectrum are the A²Π_u → X²Π_g O₂⁺ emission bands reported in the literature [15]

show the wavelengths of O₂⁺ A → X emission. The band emission agrees with A → X O₂⁺ emission. When compared with the SR bands in the literature—as shown in Figure 7—it is clear that there are several peaks (marked by arrows) that do not agree with SR band values.

Above all, there is a lack of strong evidence for the formation of a significant amount of the B state of O₂. However, the A → X O₂⁺ emission bands and dissociative charge-transfer product emissions were consistently

Figure 7. CIE spectrum of CH₃⁺/O₂: 40% beam reduction, accumulation time 10 hrs, slit width 0.5 mm. Superimposed on the spectrum are the Schumann-Runge emission bands reported in the literature [15]

observed, even when charge transfer was thermochemically unfavorable, indicating that a considerable amount of the A state of O₂⁺ can be generated during ion–O₂ collisions. Combining this with the fact that the energy difference between the A and X O₂⁺ states is close to that between the B and X O₂ states [16], a second potential mechanism can be put forward to rationalize the enhancing effect of O₂: during ion–O₂ collisions, electron transfer in the collision complex generates a significant amount of the O₂⁺ A state. During the separation of the collision complex, some of the O₂⁺ ions remain in the A state (collisional charge transfer) and emit, while others transfer charge back to the projectile, reforming O₂ in its ground state and leaving the A → X energy quantum in the projectile ion, thus allowing it to undergo O₂-enhanced dissociation. Charge-transfer reactions occur on the femtosecond time-scale. For example, the time taken for Ar to exchange charge with Ru has been calculated to be 1–2 fs [24]. The lifetime of the collision complex can be estimated from the collision diameter of the gas particles and the velocity of the projectile ion (with a kinetic energy of 8 keV) to be ~2 fs for N₂⁺/O₂, which is similar to the time taken for charge transfer.

Conclusions

Strong O₂⁺ A → X emission was observed in N₂⁺/O₂ CIE experiments due to the charge-transfer reaction between N₂⁺ and O₂. This emission band is also observed from CH₃⁺/O₂ collisions, even though charge transfer is thermochemically unfavorable in this case. It is postulated that the observed enhancement generated by O₂ for certain dissociation channels in O₂ CID experiments may result from the participation of this charge-transfer band, rather than the participation of the O₂ Schumann–Runge bands (as previously hypothesized).

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