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Citation: [The Journal of Chemical Physics](#) **89**, 4829 (1988); doi: 10.1063/1.455677

View online: <http://dx.doi.org/10.1063/1.455677>

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Chopped-laser two-photon photodissociation measurement of collisional relaxation in benzene ion

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(Received 23 May 1988; accepted 14 July 1988)

The collisional relaxation of photoexcited benzene ions was studied through two-photon photodissociation using the chopped-laser technique in the ion cyclotron resonance (ICR) ion trap. The number of collisions required for quenching varied from 1 for benzene quench gas to 95 for helium, with the quenching efficiency increasing with size and complexity of the neutral. A comparison with quenching of bromobenzene ion by many of the same quench gases showed energy transfer from benzene ion to be about a factor of 2.5 less efficient.

As understanding has grown of the role of internal energy in the fragmentation processes and reaction chemistry of gas-phase ions, the efficiency of collisional cooling of internally excited ions has been increasingly interesting. Among the ways developed for studying collisional cooling, a useful and fruitful one is based on the collisional quenching of sequential two-photon dissociation induced by a cw laser of modest power. This paper describes results for benzene-ion cooling from our ongoing study of excited-ion relaxation by this technique.

The experimental challenge in ion relaxation studies is to find a way to monitor the instantaneous internal energy of the ion as it undergoes collisional cooling from an initially hot state. A number of approaches have been used, besides the two-photon approach used here, to follow the decrease in ion internal energy as collisional cooling proceeds. Ferguson¹ and others have used the differing reactivity of different vibrational states to monitor the collisional cooling of diatomic ions, notably NO^+ and O_2^+ . Huber *et al.*² similarly used the rate variation of endothermic electron photodetachment to follow the cooling of NO_2^- . Brauman *et al.*³ found the IR multiphoton dissociation rate to depend strongly on internal energy for several ions, and exploited this effect in cooling studies. A number of studies have been directed at the collisional stabilization of metastable ion-neutral complexes.⁴ Our group has exploited the effect of internal energy on the fragmentation rate of a photoexcited ion,⁵ and has also exploited the effect of internal energy on the branching ratio for competitive photodissociation.⁶ Morgenthaler and Eyler⁷ observed the collisional quenching of vibrational hot bands in the vibrationally resolved photodissociation spectrum of hexatriene ion.

Since its discovery by Freiser and Beauchamp,⁸ the sequential two-photon photodissociation process has provided the basis for a number of collisional cooling studies.^{9,10} The two-photon photodissociation approach to studying ion relaxation essentially uses the first photon to generate an internally excited ion, and the second photon at a later time to test the extent of ion cooling. Applications of this basic strategy have been described using two successive light pulses,¹¹ using a repetitively pulsed light source,¹² and using continuous

irradiation.¹⁰ Among these three methods, the repetitively pulsed laser offers a useful combination of accuracy and experimental convenience, and we have extended its use in the present work, which is the first systematic chopped-laser study of collisional ion cooling with a variety of neutral collision partners. The ion cyclotron resonance (ICR) spectrometer provided ion trapping and detection.

In the chopped-laser approach, the ions are irradiated for a fixed length of time with a constant average light power, while the spacing between light pulses is varied. Because the extent of ion relaxation between laser pulses depends on the interval between them, the extent of dissociation varies with chopping rate in a way which can be analyzed to give the relaxation rate.

When it can be applied, the two-photon quenching approach gives reliable and unambiguous information about relaxation rates. The cooling process whose rate is measured is a well defined energy loss process in which the ion cools from the initial photoexcitation energy (2.61 eV for room temperature benzene ions at 488 nm) to the one-photon threshold (1.50 eV for benzene ions at 488 nm). The time required for cooling is determined absolutely, not relative to another competing process. Any collision partner can be used, subject to the requirement that there not be a significant ion-molecule reaction between ion and neutral. Study is limited to those ions and wavelengths for which two-photon dissociation is the only important photodissociation process. The cooling rates measured pertain to a rather high ion-internal-energy regime, since the first photon typically delivers 2–4 eV of excess internal energy.

Benzene ion, the prototype aromatic radical ion, is a particularly interesting case for studying collisional cooling. It was the first ion whose two-photon quenching was measured, but compared with a number of other ions, its rapid radiative cooling rate makes the experiments unusually hard. Freiser and Beauchamp,⁸ and van Velzen and van der Hart,¹³ both reported collisional quenching results for benzene ion in its parent gas, obtained from the pressure dependence of two-photon dissociation. Our attempts to extend these results to other quench gases (and even to obtain reproducible results for benzene quench gas) by the pressure variation method were notably unsuccessful. At the high pressures required to compete with radiative cooling, we encountered large and intractable artifacts due to collisional

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spreading of the ion cloud in the not perfectly homogeneous laser beam. This is in contrast to the study of bromobenzene ion,¹⁰ for instance, where the higher cross section permitted the use of techniques for achieving better laser-beam homogeneity, and the lower radiative cooling rate permitted operation at lower quench-gas pressures.

The chopped-laser technique for measuring two-photon quenching is free from the problem of pressure-dependent ion cloud spreading, since the relaxation rate is determined at fixed pressure. Use of this approach has been described in several studies of radiative relaxation at low pressure,¹² but it has not before been applied systematically to measuring collisional relaxation at higher pressures. Initial attempts to apply this technique to the benzene-ion system gave irreproducible results, apparently due to cell-wall heating by the laser. However, as has been described in our recent study of radiative relaxation of benzene ion,¹⁴ this artifact was reduced to apparent insignificance by illuminating the cell only during the ion-trapping period of alternate ICR cycles. With this data-collection procedure, the results were entirely well behaved and reproducible from day to day.

One of the principal motivations of the present study was to compare the quenching of benzene ion with that of bromobenzene ion, which we have reported in detail.¹⁰ Several interesting trends were noted for collisional quenching of bromobenzene ion: The quenching efficiencies of a number of small closed-shell molecules and saturated hydrocarbons correlated in a regular way with the mass of the quenching molecule and its number of internal degrees freedom (heat capacity.) In contrast, a number of quenchers with open-shell or unsaturated electronic structures had quenching efficiencies substantially above this "normal" value. This enhanced quenching probably reflects a specific chemical interaction between the bromobenzene ion and the lone-pair electrons or the π electrons of the unsaturated quench molecule. We speculated that this interaction might involve the lone-pair electrons of the bromine atom of bromobenzene. To clarify this possibility, it seemed interesting to measure the quenching efficiency of some of the same neutral molecules with benzene ion: Any dramatic difference in the pattern of quenching efficiencies could be attributed specifically to the presence or absence of the bromine substituent.

EXPERIMENTAL

The chopped-laser two-photon technique using the ICR spectrometer has been described in previous reports.¹² In this study, using the pulsed ICR spectrometer with bridge detection, benzene ions were formed by electron impact with an electron beam pulse of 10–200 ms duration at a nominal electron energy of 11–12 eV. Ions were trapped and irradiated for 3 s.

Illumination at 488 nm was with the Coherent Radiation I-12 argon ion laser, run at 2 W, focused with a 1.2 m f.l. lens to a beam diameter of ~ 2 mm. Chopping at a duty factor of 1/10 was with a set of mechanical chopper wheels ranging from 2.5 to 30 Hz, while the "infinite" chopping rate point was approximated by a fast chopper at ~ 300 Hz. The sequence of ICR pulses, with chopped illumination during alternate 3 s trapping periods, is diagrammed in Fig. 1.

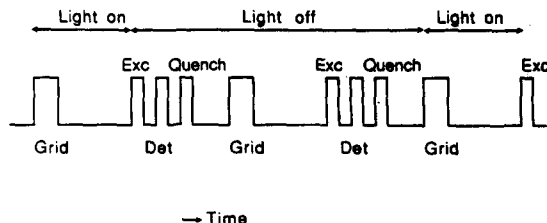


FIG. 1. Sequence of pulses and irradiation in the chopped-laser experiment.

A benzene pressure of $\sim 2 \times 10^{-8}$ Torr was used. Quench gas pressures were typically in the 10^{-6} – 10^{-5} Torr range, ranging up to 9×10^{-5} Torr for He. As discussed below, OCS and benzene quench gases were studied with a range of pressures, but for the other quench gases, a single pressure was used. In these cases, a pressure was chosen which gave a quenching rate (estimated by eye) near 50 s^{-1} , and a complete set of chopper points was taken. These data were analyzed by the usual procedure of fitting to a numerical simulation of the dissociation kinetics, to find the actual relaxation rate at the given pressure. All pressures were measured by ionization gauge, with corrections according to Georgiadis and Bartmess.¹⁵

We were concerned that the intense laser irradiation in these experiments might give significant heating of the ions. A brief kinetic analysis, summarized in the Appendix, showed this not to be a problem.

RESULTS AND DISCUSSION

For two of the quench gases, benzene and COS, the collisional relaxation rate was measured at a number of pressures, as illustrated in Fig. 2, to give assurance that the chopped-laser approach remains well behaved at high pressures and gives linear rate-vs-pressure plots. The resulting plots are shown in Figs. 3 and 4. Linearity is good even up to 4×10^{-6} Torr in the COS case. The zero-pressure intercept

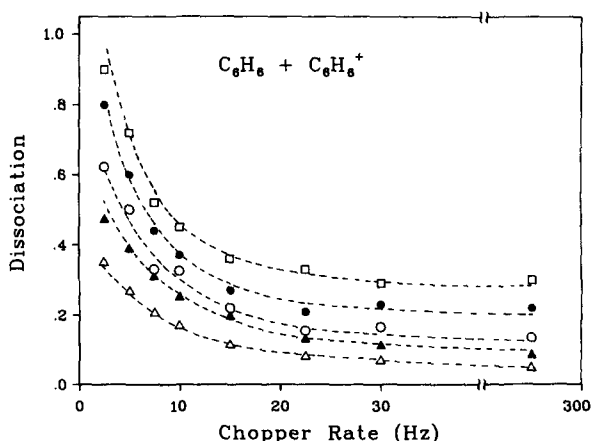


FIG. 2. Dissociation vs chopper rate at five pressures for benzene ion quenched with benzene neutral gas. The vertical axis plots the parameter $D = -\ln[(\text{light-on signal})/(\text{light-off signal})]$ for the benzene parent ion. The dashed curves are the fits to the points using the numerical simulation of the two-photon rate-process kinetics. The pressures (and the relaxation rates assigned in making the computer fits) are as follows: (\square) 2.3×10^{-7} Torr (35 s^{-1}); (\bullet) 4.7×10^{-7} Torr (45 s^{-1}); (\circ) 7.0×10^{-7} Torr (65 s^{-1}); (\blacktriangle) 1.07×10^{-6} Torr (75 s^{-1}); and (\triangle) 1.4×10^{-6} Torr (95 s^{-1}).

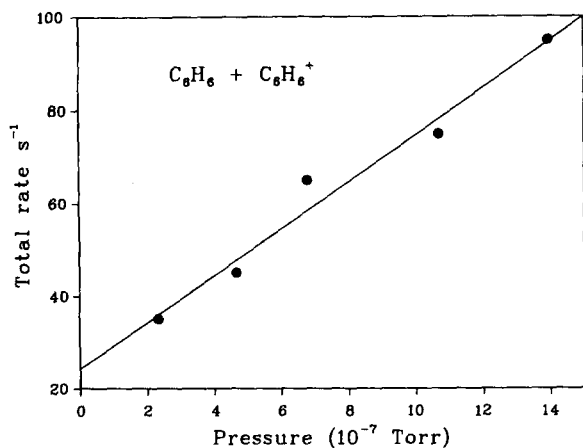


FIG. 3. Quenching rate vs pressure for benzene ion quenched with parent neutral.

(giving the radiative-relaxation rate) is 25 s^{-1} in both cases, in excellent agreement with the value of 26 s^{-1} previously reported.¹⁴ For the other quench gases, only one pressure was used.

Table I displays the results for the quench gases used. A number of other quench gases, such as ethylene, whose values would have been interesting for comparison with the bromobenzene case, could not be used because competing ion-molecule reactions depleted the benzene ion signal too rapidly. The results are reduced in the last column of the table to the collision number Z , the number of collisions required for quenching of the photoexcited ion. Z is defined as $(k_{\text{orbiting}}/k_{\text{coll}})$, where k_{coll} is the observed collisional quenching rate constant, and k_{orbiting} is the calculated rate constant for orbiting ion-molecule collisions. Z is the inverse of the frequently reported collisional efficiency for quenching.

A comparison between benzene ion and bromobenzene ion of the relative quenching efficiencies for various neutrals can be made directly from the Z values, as is shown in the first two columns of Table II. The pattern of relative efficiencies is very similar for these two ions. There is no indication of contrasting behavior for the two unsaturated quenchers, CO_2 and COS , which were among those showing enhanced quenching efficiency for bromobenzene ion¹⁰. Whatever in-

TABLE I. Benzene ion collisional quenching.

Neutral	Quenching rate constant ^a	Orbiting rate constant ^a	Collision number Z
C_6H_6	12	12.1	1.0
OCS	2.1	10.7	5
SF_6	1.4	6.8	5
CO_2	0.72	7.2	10
C_2H_6	0.62	10.6	17
CH_4	0.43	10.4	24
N_2	0.18	7.2	41
He	0.057	5.4	95

^a $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

teraction with the ion leads to efficient quenching of bromobenzene ions by these two quenchers appears to have a similar effect in benzene ion.

The two-photon quenching approach yields absolute quenching rates directly, as in Table I. A sensible comparison of absolute quenching rates between two different ions requires some care since the photodissociation thermochemistries differ: Specifically, other things being equal, a given quench neutral will give a higher quench rate for benzene ion than for bromobenzene ion, because in the former case a smaller fraction of the excitation energy must be removed by neutrals in order to drop below the one-photon threshold. For benzene ion at 488 nm, the photon energy is 2.54 eV, while the dissociation threshold is 4.04 eV, putting the one-photon threshold at 1.50 eV; thus (adding 0.07 eV of initial thermal energy to the photoexcitation energy), a photoexcited ion becomes quenched when it has lost 1.11 eV out of its initial 2.61 eV. For bromobenzene ion, the dissociation threshold is at 2.76 eV, so that at 515 nm (2.41 eV) the one-photon threshold is at 0.35 eV. In order to make comparisons among different systems, it is convenient to reduce the observed quenching rates to a calculated energy lost on the first collision.¹⁰ This is readily calculated assuming that collisional energy loss is exponential, i. e., that each collision removes fixed fraction of the current ion internal energy (in excess of thermal energy). This assumption leads to the expression

$$\Delta E(1\text{st coll.}) = E_\phi [1 - (E_T/E_\phi)^{1/Z}],$$

TABLE II. Collisional quenching comparison between benzene and bromobenzene ions.

	$Z(\text{N}_2)/Z$		$\Delta E(1\text{st coll.}) (\text{cm}^{-1})^a$	
	C_6H_6^+	$\text{C}_6\text{H}_5\text{Br}^+$	C_6H_6^+	$\text{C}_6\text{H}_5\text{Br}^+$
He	0.43	0.39	110	250
N_2	(1)	(1)	250	650
CH_4	1.7	1.8	430	1140
C_2H_6	2.4	2.9	610	1860
CO_2	4.1	3.9	1020	2400
SF_6	8.2	...	2000	...
COS	8.2	8.7	2000	4500
C_6H_6	41	...	> 8400	...

^a Calculated assuming exponential decay of internal energy from an initial photoexcited level of $20\,500 \text{ cm}^{-1}$.

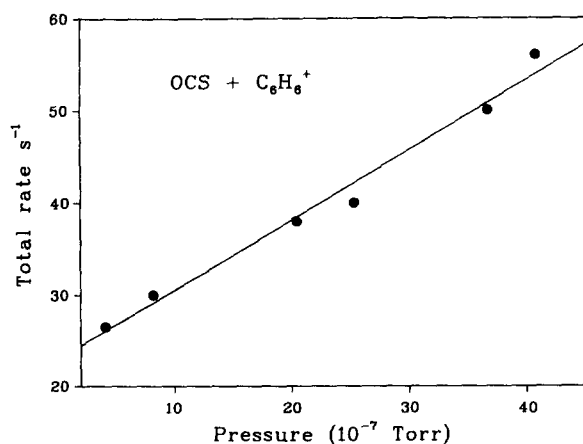


FIG. 4. Quenching rate vs pressure for benzene ion quenched with OCS.

where E_ϕ is the photon energy, and E_T is the one-photon threshold energy (corrected for the equilibrium ion thermal energy, 0.07 eV in the case of benzene ion).

These values are compared for benzene and bromobenzene ions in the last columns of Table II. Benzene ion quenching is consistently about 40% as efficient as bromobenzene ion quenching with the same quench gas. Thus the presence of the bromine atom appears not to have a specific effect on quenching by particular gases, but does seem to enhance the quenching interaction uniformly by a factor of 2.5 for a variety of quenchers. The higher efficiency for bromobenzene ion might be a result of the dipole moment, the higher polarizability, or the lower vibrational frequencies of bromobenzene ion, the extended lone-pair electrons of the bromine atom, or the longer duration of collisions in the heavier system, or some combination of these factors.

CONCLUSION

The chopped-laser two-photon technique as applied here gives excellent results in measuring the quenching efficiency of even very inefficient quench gases, and is probably the method of choice for observation of two-photon quenching. The results presented for benzene ion quenching follow the expected trends, with the efficiency increasing dramatically with increasing size and complexity of the neutral partner. The lower absolute energy transfer rates in comparison with bromobenzene emphasize the important role of the ion in controlling the energy transfer efficiency, although it is not yet clear what specific property of bromobenzene ion makes it so much better an energy donor.

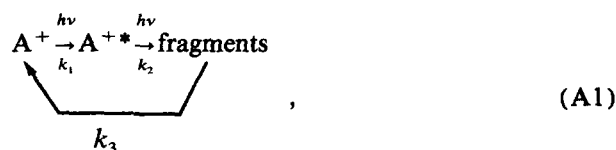
ACKNOWLEDGMENTS

The support of the National Science Foundation, and of the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

APPENDIX: EXTENT OF LASER HEATING OF THE ION POPULATION

In the case of benzene-ion two-photon dissociation at 488 nm, the one-photon threshold is very high (1.50 eV), and we may be concerned that the "relaxed" ions may still have significant average superthermal internal energy. If the ion population is in fact heated substantially above ambient temperature by the laser, the kinetic analysis for extracting relaxation rates from two-photon quenching data is no longer correct. We show here that this was not the case in the present experiments.

A full kinetic analysis of this situation is unnecessarily complex, and a rather simple approximate analysis will be both clear and sufficient. The two-photon kinetic scheme is



where A^+ is the parent ion, A^{+*} is the hot parent ion (lying above the one photon threshold), k_1 and k_2 are the rate constants for first and second photon absorption, respectively; and k_3 is the relaxation rate. As usual, we will set $k_1 = k_2$.

Under steady laser irradiation, after a brief initial transient has died out, the A^+ concentration declines exponentially with a rate constant which we will call k_d :

$$[A^+] = [A^+]_0 e^{-k_d t} \quad (A2)$$

The photoexcited A^{+*} ions relax back toward ambient temperature with the rate constant k_3 . Average laser heating of the ion population will be significant if a typical ion is re-excited by absorption of a new photon before it has thoroughly relaxed, that is if k_3 is not much greater than k_1 . Straightforward manipulation of the solution of kinetic scheme (A1) leads to the simple approximate relation

$$\frac{k_1}{k_3} \cong \sqrt{\frac{k_d}{k_3}},$$

so the condition $k_1 \ll k_3$ is equivalent to the condition $\sqrt{k_d/k_3} \ll 1$. This latter expression is convenient because k_d and k_3 are both quantities measured directly in the experiment.

In the present experiments, k_d was of the order of 0.1 s⁻¹, and k_3 was of the order of 40 s⁻¹. Therefore $\sqrt{k_d/k_3}$ was of the order of 0.05, which is much smaller than unity, and we conclude that laser heating of the ion population was negligible.

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