PROSPECTS FOR LASER-INDUCED PROCESSES IN COLLISIONS : A ROUND TABLE

R. Berry

JOURNAL DE PHYSIQUE
Colloque C1, supplément au n°1, Tome 46, janvier 1985

PROSPECTS FOR LASER-INDUCED PROCESSES IN COLLISIONS : A ROUND TABLE

R.S. Berry

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, U.S.A.

Résumé - La discussion qui conclut le Colloque, à propos des directions futures possibles du domaine de recherche, est résumée ici.

Abstract - The concluding discussion of the Colloquium is summarized, concerning possible future directions for the field.

The concluding session, chaired by R. Stephen Berry, was a time for perspective and speculation. Some of the discussion is summarized here.
The first subject, raised by Jacob Leventhal, was concerned with the extensively studied associative ionization process in sodium :

$$Na(3p) + Na(3p) \longrightarrow Na_2^+ + e \ , \qquad /1/$$

and the possible laser-assisted process :

$$Na(3s) + Na(3s) + 2\hbar\omega \longrightarrow Na_2^+ + e \ , \qquad /2/$$

where ω is close to the 3s ——> 3p resonance frequency. J. Leventhal reported on recent experimental investigations on this problem. He concluded that, at high laser intensities, the observed off-resonant production of Na^+ and Na_2^+ ions is essentially due to the presence of the neutral dimers Na_2 (see below the short contribution submitted on this subject).

William Happer pointed out the potential for spin polarization studies by optical pumping and collisional exchange. Much of this process can be expressed in terms of analogies with electrical circuitry, particularly with resistance and capacitance. If an analogue can be found for inductance--possibly long-lived collision complexes would be appropriate--then one could begin to think of analogues of resonant circuits. J. Lukasik noted that of the five proposals made several years ago by S. Harris, laser-induced spin exchange was one that had not yet been observed.

On a related topic, Michel Barat mentioned the new high-resolution, high-intensity source of electrons developed by Roger Azria and his group at Orsay, based on the surface ionization approach of Robert Celotta and his collaborators at NBS. With the enormous currents these sources provide, one will have the capability to study electron scattering resonances much more effectively, and in particular to try to observe optical transitions between those resonances. The importance of such transitions had been emphasized by the session chairman at the Pisa meeting, the predecessor to this one.

A subject getting increasing attention from theorists that has yet to be explored by experimenters was raised by Thomas George ; this is the possibility of lengthening collision lifetimes by using laser radiation to couple states, especially (but not necessarily) to couple bound and free states. Others who have also done theoretical work in this area include A. Lami and N.K. Rahman, K. Burnett and B.J. Dalton. The sorts of studies that lifetime extension by radiative coupling (LERC?) would include are optical studies of resonance-resonance transitions and enhanced cross sections for ionization of collision complexes. One could perhaps imagine coupling

heavy-particle systems radiatively for intervals long enough for energy to flow from one vibrational mode to another, and, in particular, from the "reaction coordinate" to other vibrational modes, leading to very great enhancement of lifetimes of poly-atomic collision complexes. This line of reasoning could apply to radiatively perturbed dielectronic recombination as well. In either case, radiatively enhanced inverse predissociation or radiatively enhanced dielectronic recombination, the lifetime enhancement by radiation only serves as a sort of catalyst, to extend the lifetime of the compound state while all the distances are comparable to the impact parameter, for a period long enough for other, slower intramolecular relaxation processes to provide long-time stabilization. As Benoit Soep pointed out, van der Waals molecules are compounds with large internal separations and can be thought of as corresponding to species trapped in bound states at distances large with respect to conventional chemical bonds but not so very large compared with the full range of impact parameters within which reactions can occur. These molecules thereby give us probes of the behavior of reactive systems at intermediate distances.

Paul Berman reviewed those bound-state properties in radiation fields which are related to laser-induced phenomena in collisions. Among them are 1) forbidden transitions whose selection rules are broken by electromagnetic fields ; 2) second-harmonic generation in centrosymmetric systems, in which the radiation field is again a symmetry-breaking device ; 3) the generation of optical coherence by a medium ; 4) reactions of atoms with or on surfaces, induced by radiation, and 5) the production of femtosecond pulses of radiation by extreme mode locking. Ingolf Hertel pointed out the use of two-level coherences as the analogues of double-slit diffraction experiments.

Jacques Lukasik reminded the audience of some experiments carried out in Palaiseau on laser-assisted collisions in molecules, namely in carbon monoxide. They involved high-energy (E ~ 11 eV) Rydberg states of CO and led to the observation of laser-assisted collisions with cross-sections larger than 10^{-16} cm^2 at the laser intensities approaching 10^{10} W/cm^2. The transfer of about 2 % of the initial state population to the final level turned out to be too small for a coherent, stimulated emission. Only spontaneous VUV fluorescence in the 1150-1180 Å was observed. The large cross sections achieved in these experiments establish, however, the feasibility of such processes for future applications, as for example, exciting vacuum ultraviolet lasers.

Jean-Louis Picqué emphasized the interest of electron spectrometry for the study of laser-induced effects in ionizing collisions. In connection with the problem raised by J. Leventhal, he pointed out that, for off-resonant high-intensity irradiation of sodium, it should be possible to discriminate between laser-assisted collisional ionization and photoionization involving Na_2 dimers since these processes give rise to different electron energies. Investigations along these lines have already been done in the LURE experiment (using the set-up described in the paper by B. Carré et al.).

Jean-Louis Picqué and Raymond Vetter reported on work in progress at Laboratoire Aimé Cotton on the reaction :

$$Cs + H_2 \longrightarrow CsH + H, \qquad /3/$$

responsible for the formation of the so-called "laser snow" in bulk phase experiments. This reaction has been observed very recently under single-collision conditions in a crossed-molecular beam apparatus. In order to balance the 2.7 eV endoergicity of the process, Cs atoms were excited to the 7p level with a first laser. A second laser was used to detect CsH in various rotational levels, via laser-induced fluorescence. In the case of formation of a transition state, laser-assisted effects could also be observed in this system.

Finally (structurally, not temporally) Keith Burnett posed the caution that we should be careful not to limit ourselves only to the information provided by probing

collision complexes with photons. He reminded the participants of the importance of comparing all the possible probes and selecting the most appropriate, not necessarily (editor's words) the most fashionable among them.

Appendix : Has laser-induced associative ionization been observed in Na(3s)-Na(3s) collisions ?

Charles E. Burkhardt and Jacob J. Leventhal
University of Missouri
St Louis, Missouri 63121, USA

One of the most intriguing of the reported "laser-induced" reactions is the two photon associative ionization process :

$$Na(3s) + Na(3s) + 2\hbar\omega \longrightarrow Na_2^+ + e \qquad /1/$$

In this reaction both photons have the same wavelength, a wavelength that is close to, but not coincident with, the D-lines. Last year at this conference, Dr M. Allegrini of the CNR Laboratory in Pisa reported results of experiments performed in collaboration with our group at the University of Missouri-St Louis. We mass analyzed ions formed in laser-irradiated sodium vapor ($\sim 10^{12}$ cm^{-3}) and found Na^+ and Na_2^+ at all wavelengths in the approximate range 5850-6000 Å. However, the expected enhancements of these ion signals at the D-lines were not observed. [Enhancement of the Na_2^+ signal was expected to result from Na(3p)/Na(3p) associative ionization and that of Na^+ from resonance-enhanced three photon ionization of Na(3s)]. The data led us to conclude that these ions were produced by multiphoton processes involving the inevitably present (neutral) dimer component of the vapor. We were unable to ascribe any Na_2^+ formation to reaction /1/.

In the intervening time we have refined the apparatus and reexamined the situation using a laser of much narrower bandwidth ($\Delta\lambda \tilde{\sim} 0.1$ Å). We report the following observations :

1. At low laser power density, Na_2^+ are formed only at D-line wavelengths and are due entirely to Na(3p)/Na(3p) associative ionization--Na^+ was not observed at any wavelength.

2. As the laser power density is increased, comparable signals of Na^+ and Na_2^+ appear at off resonant (non D-line) wavelengths, and both signals depend strongly on laser power density (a power greater than 2).

3. At sufficiently high laser power density, the ion signals in the highly structured spectra are sufficiently strong to obscure ions produced by Na(3p) (at the D-lines), consistent with the data reported last year at this conference.

4. The features of the Na^+ and Na_2^+ spectra occur at precisely the same wavelengths with the exception of the D-lines, where Na^+ is relatively weak.

Analysis of the data lead us to conclude that the off-resonant production of ions is indeed due to the presence of the neutral dimers. We suggest that the ions are produced by two-photon resonant absorption by Na_2 followed by (single photon) photoionization. Any lack of correlation between the features of the three photon produced ion spectra and two photon absorption spectra of Na_2 does not preclude the dimers as the source of the ions and infer the occurence of reaction /1/. If any Na_2^+ are produced by reaction /1/, their identification as such is equivocal at best due to the presence of the dimers.

We propose that if true laser-induced associative ionization is to be observed, then the best candidates for study are rare gas systems such as :

$$He(1s^2\ ^1S) + He(1s2s\ ^3S) + \hbar\omega \longrightarrow He_2^+ + e \ , \qquad /2/$$

where the wavelength of the photon in reaction (2), though close, does not correspond to any atomic helium transition.