

ADDITIONS AND CORRECTIONS

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Kolja Paech, Rebecca A. Jockusch, and Evan R. Williams*: Slow Infrared Laser Dissociation of Biomolecules in the Rapid Energy Exchange Limit

Page 9763. In our recent publication, we omitted the photon energy ($h\nu$) from the energy balance condition of a steady-state population. The correct steady-state condition is

$$\sum_{\nu} B(\nu)\rho(\nu)P(\nu)h\nu = \sum_{\nu} [A(\nu) + B(\nu)\rho(\nu)] P''(\nu)h\nu \quad (1)$$

All subsequent calculations are as described previously. Carrying through the correction of eq 1 leads to the following modification of eq 10

$$\frac{d \ln \rho_{\text{relative}}(\nu_{\text{laser}})}{d(1/T)} = - \frac{d}{d1/T} \ln \left(\sum_{\nu'} [v' B(\nu') \rho(\nu') - v' A(\nu') P''(\nu', T)] - v' A(\nu_{\text{laser}}) P''(\nu_{\text{laser}}, T) \right) \quad (10)$$

Applying eq 10 as described, the resulting parametrized Arrhenius-like equation has a proportionality constant s with an absolute value that is $\sim 10\%$ greater than previously reported. The corrected relationship for the slow IR laser dissociation of peptides and proteins (eq 11) becomes

$$\frac{d \ln k}{d \ln \rho(\nu_{\text{laser}})} = 4.34 E_a \quad (11)$$

Because the energies of vibrational transitions vary by about a factor of 70 (from 50 to 3500 cm^{-1}), the practical significance of omitting the photon energy from eq 1 is that, in our previous calculations, the effect of emission at higher frequencies was systematically underestimated. Using the corrected version of eq 11, activation energies for several peptides and proteins derived from laser photodissociation data, and their comparison to BIRD measurements, are as seen in the table.

compound	charge state	E_a (BIRD)	E_a (laser)	error (% , this work vs BIRD)
leucine enkephalin	1+	1.1 ^d	1.20 ^c	+9
bradykinin	1+	1.3 ^d	1.28 ^a	+2
bradykinin	1+	1.3 ^d	2.14 ^e	+66
bradykinin	2+	0.8 ^d	1.0 ^a	+25
melittin	2+		1.4 ^f	
melittin	3+	1.76 ^g	1.4 ^f	
ubiquitin	5+	1.6 ^h	1.7 ^e	+6
ubiquitin	11+	1.2 ^h	1.3 ^e	+8

Data sources are as published previously. All notation is as previously defined.

Other calculations presented in this publication (internal energy distribution of a laser-heated population, relative emission rates as a function of frequency) are independent of the modifications outlined above and remain as published.

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